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TECHNOLOGY UTILIZATION

ADHESIVES, SEALANTS, AND GASKETS

A SURVEY



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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Foreword

The Administrator of the National Aeronautics and Space Administration established a technology utilization program to accelerate the dissemination of technical information developed for space missions. This survey is part of that program. Previous volumes have described valves, inorganic coatings, solid lubricants and other devices and materials that have been improved or developed to meet NASA's requirements.

Adhesives, sealants and gaskets have been developed to operate in the extreme environments encountered in space work. NASA research centers have encouraged these developments, helped to evaluate them, and sponsored fundamental studies of polymers that may facilitate further advances. This survey of such contributions to the technology of adhesives, sealants and gaskets was made by the Southern Research Institute.

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Needs and Developments

Operations of NASA have created needs for adhesives, sealants, and gaskets that perform reliably under wide ranges of adverse environmental conditions. In the construction of spacecraft and rocket engines, the use of structural adhesives, rather than mechanical fasteners or welding, makes possible great savings in weight (ref. 1), a critical factor in space technology. Sealants are used occasionally to close small openings or crevices in structures, and gaskets are used in sealing many types of closures in the spacecraft rockets.

Reliability is a foremost criterion for spacecraft structures, and the adhesives, sealants, and gaskets used must function without failure under extreme environmental conditions. Materials must function, for example, under the conditions encountered in fuel tanks at temperatures as low as -250°C . Development of materials that can be used in a liquid oxygen environment has been of particular concern to NASA.

The technologists at the NASA Centers and NASA's contractors have cooperated closely with manufacturers of adhesives, sealants, and gaskets and have encouraged these industries to develop new and improved materials to meet NASA's requirements. That NASA's operations have provided markets for improved materials, has, in itself, encouraged new developments; and NASA's cooperation in evaluating new products offered by industry has been of at least equal importance in spurring technological progress. This approach to new product development has the advantage of being an economical method for obtaining improved materials.

NASA has taken full advantage of research carried out by industry and by other agencies of the U.S. Government, supplementing this only when necessary with its own research directed to improving available products. NASA, however, has also considered future needs and has conducted and sponsored, under contract, fundamental research on new polymers. It seems likely that this fundamental research will ultimately be NASA's most significant contribution to the technology of adhesives, sealants, and gaskets. For this reason,

this survey includes discussions of fundamental polymer research that is believed to be pertinent.

Many of the research programs were undertaken with a very specific objective, so only a single property (for example, low-temperature flexibility) may have been examined in the screening evaluation of the compositions that were developed. Thus, it is possible that many compositions that would be of interest for use in less rigorous environments have been discarded because they would not be serviceable at an extremely low temperature, or under some other equally specialized environmental condition.

In the following separate reviews of NASA's research and development programs on adhesives, sealants, and gaskets, an attempt has been made to present sufficiently detailed information on the results obtained to indicate the promise of the various approaches to the production of new and improved products by industry. The original reports and publications should, of course, be consulted for full details. The following items appear to be of special potential interest for industrial use.

Polymeric fillers in adhesives.—The study of fillers for epoxy-polyamide adhesives described in Chapter 2 showed that finely ground nylon was superior to the inorganic fillers evaluated. This technique may be of general utility and possibly can be used to advantage in various types of adhesives.

Elastomeric films in glue lines.—The benefits resulting from the incorporation of an elastomeric film in adhesive glue lines was demonstrated in the investigation described in Chapter 2. The results of this work show that with proper selection of film and adhesive this technique provides an excellent means for distributing stresses within a glue line.

Epoxy ester adhesives.—Several interesting epoxy ester type adhesives are described in Chapter 2. More detailed evaluation of these adhesives could disclose properties of interest for industrial adhesives.

Sealants for low-temperature service.—Two elastomeric sealants suitable for service at very low temperatures are described in Chapter 3.

Gasket design.—A novel gasket design that utilizes the mechanical recovery properties of glass fabric is described in Chapter 4. This gasket is a laminate of plastic sheet and glass fabric in which the fibers in the glass fabric are only partially surrounded by plastic.

Measurement of stress in gaskets.—A miniature stress transducer that could provide a means for monitoring the stress in installed gaskets is discussed in Chapter 4.

Adhesives

Adhesives are used in NASA's programs in many ways. The principal uses are in metal-to-metal bonding and in bonding plastics, such as honeycomb, to metal. The use of adhesives rather than rivets, bolts, or welds makes possible a reduction in weight (ref. 1). When joints are made with adhesives, the stresses at joints are distributed rather than concentrated, as they are in the case of riveted joints, for example, and, therefore, thinner sections of metal can be used. Brackets, reinforcing panels and auxiliary equipment can be attached with adhesives to major structures without disturbing the structure and thereby risking development of a weak spot.

Apparently, most of NASA's work that has been done with adhesives for bonding materials other than metals has been in connection with the development or construction of specific items, and information on adhesives was not specifically identified. In many of the adhesive-bonded items manufactured for NASA, the selection of the adhesive apparently has been left to the manufacturer subject only to the requirement that the bonds conform to specifications set by NASA. Accordingly, almost all of the information on adhesives reviewed in this survey relates to those for bonding metals.

Most of the adhesives used by NASA have been proprietary products, and the compositions of these products are seldom disclosed by the manufacturers beyond an indication of the general class of polymer involved. At the time this survey was made, urethane and epoxy polymers (including the so-called modified epoxies) were the most extensively used base materials for the adhesives.

The epoxy-type adhesives that are commercially available as a result of extensive research and development by industry and various governmental agencies have proven to be generally satisfactory structural adhesives for use when extremes of temperature are not encountered. Commercial epoxy adhesives are available that will withstand extended exposure to 150° C without excessive loss of adhesive bonding strength, and some will perform satisfactorily for

short periods at even higher temperatures. However, the epoxy adhesives that are satisfactory at high temperatures are not very satisfactory at low temperatures, such as those encountered in handling LOX and liquid hydrogen. Commercial nylon-epoxy and polyurethane adhesives have shown promise as adhesives for very-low-temperature service, but they are not satisfactory for use at temperatures of about 150° C and higher. The research on adhesives that has been carried out by NASA has been directed mainly to the development of adhesives for very-low-temperature service, adhesives for high-temperature service (250° C and higher), and adhesives that will perform satisfactorily at both extremes of temperatures. NASA-sponsored research on adhesives prior to about 1963 was concerned chiefly with adhesives for low-temperature service. NASA has sponsored only limited research on adhesives for use at high temperatures. Other governmental agencies have been very active in this field and the information they developed was available to NASA (refs. 2, 3, 4, 5, 6, and 7). Recently NASA has sponsored research with the object of developing adhesives that will perform satisfactorily at both very low and fairly high temperatures (−250° C to +200° C).

Research programs have had very specific goals, and much of the research has involved modification or evaluation of proprietary materials, the composition of which was not generally known. For example, a program concerned with developing an adhesive suitable for use at cryogenic temperatures involved the preparation of a large number of experimental adhesives, many of them apparently novel compositions. Each of these compositions was subjected to preliminary evaluation, but any adhesive that did not have satisfactory properties at liquid nitrogen temperature (−193° C) was not evaluated further. The validity of this approach for reaching a specific goal with minimum effort is beyond question, but such an extremely limited evaluation does not provide an adequate basis for appraising the commercial utility of the experimental products.

NASA research on adhesives is best reviewed by considering each individual major program separately, since the objective of each of these programs was basically different. Some of the NASA programs were designed to provide solutions to specific problems of immediate interest and others had longer range objectives. The scopes of the evaluations carried out in the various programs were different, and so it was not feasible to attempt to make direct comparisons of the test data obtained.

It is not appropriate in this review to present details of testing procedures that are fairly standard in concept, but a general discussion of evaluation procedures is given below to provide orientation. The numerical values obtained in the evaluation of any given adhesive

might be influenced by many minor factors in procedure that were not always defined; hence, caution should be exercised in making direct comparisons of values obtained in different laboratories.

Unfortunately, there is no single test that can be used to evaluate an adhesive. The strength of the adhesive bond obtainable with the adhesive is a matter of prime consideration, but there are many different types of strength to be considered. The two types of strength most commonly measured in evaluating adhesives are tensile shear strength and peel strength (commonly called T-Peel strength) of the bonds. The mechanical aspects of these two tests are illustrated in figure 1 with the straight arrows indicating the direction of stress.

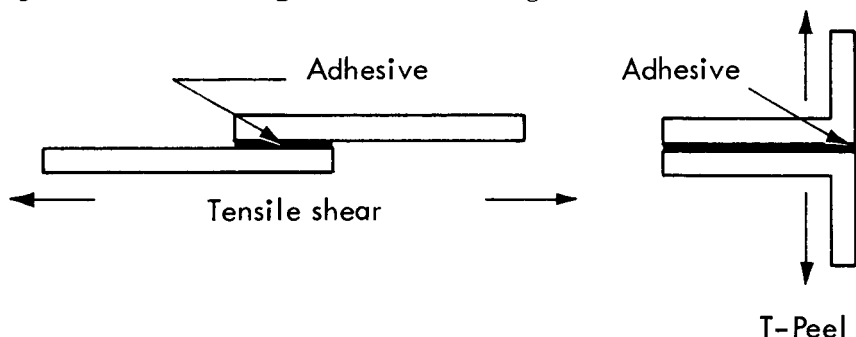


FIGURE 1.—Mechanical aspects of the tensile-shear and T-Peel strength tests for adhesive bonding

In either test, failure of the bond may occur by either adhesive failure at the interface or by cohesive failure in the body of the adhesive itself. If adhesive failure occurs at the interface, then variations in the method of preparation of the surfaces of the substrates may have a major effect on the results of the test. Roseland has reported tensile shear and T-Peel test data for a number of commercial adhesives (ref. 8) and his data (table I) illustrate the range of properties obtainable with these products.

Although tensile-shear and, less frequently, T-Peel tests were used as the main screening tests in the evaluation of experimental adhesives, the data obtained from these tests provide only a limited basis for appraisal of the merits of the adhesives. Many other properties are of equal or even greater importance to many of the potential users of adhesives. Such properties as resistance to thermal shock, resistance to vibration and impact, and creep characteristics are of crucial importance in many applications. Maintenance of strength properties on aging, sensitivity of the adhesive bond to surface preparation, pot life of the adhesive, and ease of application are important considerations in almost all applications for adhesives (refs. 9 and 10).

TABLE I.—*Tensile-Shear and T-Peel Strengths of Selected Commercial Adhesives*

Adhesive	Tensile-shear strength, psi		T-Peel strength, lb/in	
	−253° C	121° C	−253° C	121° C
Modified epoxy.....	1233	293	2.0	4.5
Flexibilized epoxy.....	2485	555	1.9	3.9
Polyamide epoxy.....	2135	292	4.9	5.5
Nylon-filled epoxy.....	1706	173	4.8	4.4
Polyurethane.....	5463	201	<100	4.7
Nylon-epoxy.....	1467	1950	10.5	37.8
Modified epoxy and nylon cloth..	1553	2704	13.0	13.0

ADHESIVES FOR VERY-LOW-TEMPERATURE APPLICATION

The Narmco Research and Development Division of Whittaker Corp. carried out for the George C. Marshall Space Flight Center an extensive research program on adhesives for use at very low temperatures (refs. 11, 12, 13, and 14). In the course of this program, they studied the effects of adhesive composition, fillers, surface preparations, and other significant variables on the performance of nylon-epoxy base adhesives.

The program was started in April 1961 and continued through April 1963. First the literature was surveyed to identify the types of adhesives that offered the most promise of satisfactory performance at very low temperatures and that would be suitable for use with only the facilities found in the field. To satisfy this latter requirement, the techniques of surface preparation and bonding had to be simple, and bonding and curing had to be obtainable at ambient temperatures and with low bonding pressure.

This literature survey identified 31 commercial adhesives of potential utility at low temperatures and for which some test data were available (ref. 14, Sec. IV). A review of the data indicated that the most promising types were the nylon-epoxy, the epoxy-polyamide, and the polyurethane adhesives. The nylon-epoxy adhesives, as a class, had extremely high tensile-shear strength at low temperatures but they required a high temperature (about 150° C) for bonding. The epoxy-polyamides had the advantages of ease of bond preparation and moderate curing conditions. The polyurethanes were unique in showing a pronounced gain in strength when the temperature was lowered from room temperature to −193° C. The other types of

adhesives considered were judged less satisfactory for various reasons, such as low strength (particularly at low temperatures), or the need for elaborate bonding procedures. The data of figure 2 show the tensile-shear strengths for several of the commercial adhesives that were investigated.

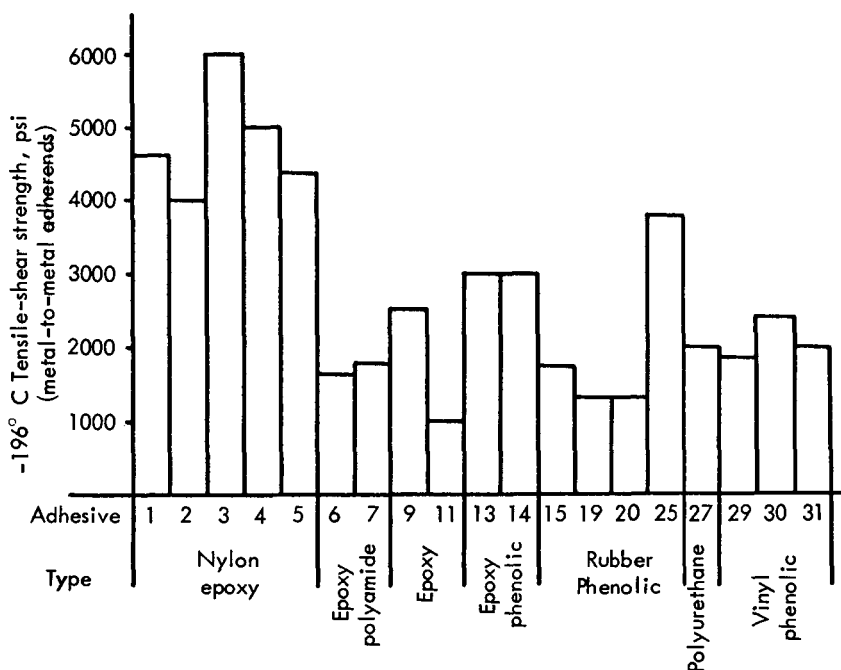


FIGURE 2.—Tensile-shear strength of commercial adhesives at -196°C .

New Adhesives

Six adhesives suitable for use at very low temperatures were developed in this program, and comprehensive evaluations of these adhesives were made (ref. 14, sec. XXII). Descriptions of these adhesives follow.

Adhesive A is a two-component system consisting of a nylon-filled epoxy resin and a nylon-filled polyamide curing agent. The novel feature of this adhesive is the use of nylon as a filler. Nylon was the only material of the several investigated that was effective for improving the low-temperature performance of the epoxy-polyamide type adhesive.

Adhesive B is a three-component system that includes 1-mil Teflon FEP (Type 544) film, an epoxy resin, and a polyamide curing agent. Adhesive bonds are made by: (1) mixing the epoxy resin

and polyamide to form an adhesive, (2) spreading this adhesive onto the metal substrates to be bonded and onto both sides of the Teflon films, (3) placing the coated films, one atop the other, over one substrate, and (4) pressing the parts together. A glue-line thickness of 5-8 mils is optimum. In the development of this adhesive, several types of film material, both polymeric and metallic, were evaluated and, of these, only the Teflon FEP film was found to be effective in improving low-temperature performance.

Adhesive C consists of Adiprene L-100 (a polyurethane) cured at room temperature with MOCA (4,4'-methylene-bis(2-chloro-aniline). The MOCA is melted and mixed with the Adiprene, in the ratio of 100 parts of Adiprene and 11 parts of MOCA, just prior to use. The adhesive is characterized by ease of use and by good strength and toughness at low temperatures.

Adhesive D consists of Adiprene LD-167 (a polyurethane) cured with MOCA. Prior to use, 20 parts of molten MOCA is mixed with 100 parts of Adiprene LD-167. This adhesive cures faster than Adhesive C.

Adhesive E utilizes the Adiprene L-100 and MOCA mixture described above as Adhesive C. This adhesive mixture is troweled onto a 181-112 glass fabric, and the coated fabric is pressed between the surfaces to be bonded. The glass fabric improves the strength of the bond at very low temperatures.

Adhesive F is simply a sheet of Teflon FEP used as a hot-melt adhesive and bonded at 372° C.

These six experimental adhesives were evaluated extensively. The tensile-shear strengths and the T-Peel strengths of these adhesives at temperatures ranging from -253° C to 82° C are given in tables II and III. The test specimens used were made of 7075-T6 aluminum alloy. The surfaces to be bonded were etched by the standard Forest Products Laboratory sodium dichromate-sulfuric acid etching process. The epoxy-polyamides and polyurethane adhesives (A through E) were cured at room temperature under contact pressure. Adhesive F, the Teflon hot-melt, was bonded at 370° C with 15 psi pressure.

The polyurethane adhesives (C, D, and E) exhibited outstanding tensile-shear and T-Peel strengths at very low temperatures and had satisfactory strengths at room temperature. Comparison of Adhesives A and B is interesting. Both of these adhesives are of the epoxy-polyamide type but Adhesive A is a nylon-filled material and Adhesive B has two thin (1 mil) sheets of Teflon FEP incorporated in the glue line. Adhesive B is significantly superior to Adhesive A in strength at low temperature, indicating that the technique of embedding flexible films in the glue has considerable merit.

TABLE II.—*Tensile Shear Strengths of Narmco Experimental Adhesives*¹

Adhesive	Cure time, days ²	Tensile-shear strength, psi					
		−253° C	−196° C	−55° C	R.T. ⁶	52° C	82° C
A.....	7-15	2552	2710	3782	3127	1515	544
B.....	8-16	5352	³ 5090	3827	1972	1328	738
C.....	8-18	⁴ 8050	³ < 5005	4662	1578	762	454
D.....	7	³ < 6725	³ < 5198	³ < 5085	1960	852	353
E.....	7	6525	³ 5258	4542	1073	660	406
F.....	(⁵)	4966	2775	2200	1120	941	801

¹ Specimens: 0.064-in. 7075-T6, bare aluminum-alloy breakaway panels with sodium dichromate-sulfuric acid etch, bonded with contact pressure (except where noted) with ½-in. overlap. Tested per MIL-A-5090D. Averages of four specimens.

² At room temperature, except Adhesive F.

³ Failure in adherend gripping holes.

⁴ Doublers used on gripping ends of specimens.

⁵ 15 min at 370° C.

⁶ Room temperature.

TABLE III.—*T-Peel Strengths of Narmco Experimental Adhesives*¹

Adhesive	Cure time, days ²	T-Peel strength, lb/in.					
		−253° C	−196° C	−55° C	R.T.	52° C	82° C
A.....	7-17	3.0	3.0	4.0	3.9	9.0	2.0
B.....	8-18	6.3	9.0	7.5	3.6	8.5	2.0
C.....	8-18	26.0	33.0	22.5	11.3	9.0	10.0
D.....	7-25	26.0	22.0	9.5	30.0	9.0	9.5
E.....	7-25	44.0	46.0	14.0	20.0	13.0	11.0
F.....	15 min at 370° C.	38.0	38.0	14.0	4.0	2.5	1.2

¹ Specimens: 0.020 in. 7075-T6 bare aluminum 1×12-in. strips with sodium dichromate-sulfuric acid etch, bonded with contact pressure (except where noted).

² At room temperature, except Adhesive F.

A comparison of the properties of Adhesive C and Adhesive E, which differed by the inclusion of the glass fabric in Adhesive E, shows that substantial improvements in T-Peel strength at all temperatures resulted from inclusion of the glass fabrics. None of these experimental adhesives had good strength properties at temperatures much above room temperature.

The impact strengths of the experimental adhesives and two selected commercial adhesives were measured at -196°C and at room temperature according to Methods 1051 and 1051.1-T of Federal Test Method Standard No. 175. The metal test specimens were constructed of 7075-T6 aluminum. The data obtained (table IV) show that Adhesive C, a polyurethane, had excellent impact resistance at both temperatures and, as indicated above, this adhesive also had superior tensile-shear and T-Peel strengths at low temperatures. The low impact strength of Adhesive B, which was prepared with an epoxy-polyamide adhesive and two layers of Teflon film in the glue line, is somewhat surprising. The inclusion of the Teflon resulted in substantial improvements in tensile-shear and T-Peel strengths but produced a drastic loss in impact resistance. Adhesive A, which did not show outstanding strength properties, had excellent impact resistance. Butt tensile strengths were determined by Method 1011.1 of Federal Test Method Standard No. 175. The metal test specimens were constructed of 7075-T6 aluminum. The results of this evaluation (table V) are quite significant because at -253°C the test specimens bonded with Adhesives B, C, and D broke in the aluminum and not at the adhesive bond. Even at -196°C , the test specimens bonded with Adhesives C and D broke in the aluminum before the adhesive bond failed.

Additional evaluations were made of Adhesives A, B, and C, which were judged to be of particular interest. Repeated thermal shock did not adversely affect the strength of bonds made with any of these adhesives when they were subjected to 20 cycles of rapid temperature change from room temperature to -196°C . Post-curing bonds

TABLE IV.—*Impact Strengths of Experimental Adhesives and Selected Commercial Adhesives*

Adhesive	Cure time, days ¹	Impact strength, ¹ ft-lb/in.	
		-196°C	R.T.
A.....	3	10.7	14.4
B.....	3	0.7	2.6
C.....	3	13.2	12.6
D.....	6	1.1	3.1
Metlbond 406.....	(²)	3.2	10.1
E.....	5	14.1	3.1
Resin 3135/7111.....	3	1.8	19.0

¹ At room temperature, except Metlbond 406.

² 15 minutes at 177°C .

TABLE V.—*Butt Tensile Strengths of Narmco Experimental Adhesives*¹

Adhesive	Cure time, days ²	Butt tensile strength, psi					
		−253° C	−196° C	−55° C	R.T.	52° C	82° C
A-----	8-9	5700	5470	3930	3200	1250	774
B-----	8-16	³ 9200	6100	3180	1900	1655	1000
C-----	7-15	³ 7600	³ 6240	5800	1860	1000	610
D-----	9-10	³ 6800	³ 7700	6360	1910	820	749
E-----	3-7	6200	5930	4150	795	585	470

¹ Specimens and test: Federal Test Method Standard No. 175, Method 1011.1. Surface preparation: Sodium dichromate-sulfuric acid etch. Cure: Contact pressure.

² At room temperature.

³ Failure in aluminum.

made with Adhesives A, B, and C for 1 hour at 93° C increased the tensile shear strengths of Adhesives A and B, but had no effect on the strength of Adhesive C. The post-cure produced some improvement in the T-Peel strengths at −196° C of the three adhesives.

The data obtained in these evaluations show that some exceptionally effective new adhesives for use at very low temperatures were developed in this program.

Studies of Nylon in Adhesive Systems

A significant part of the Narmco program was concerned with studies of the use of nylons in adhesives. These studies included an investigation of the effects of processing variables on the properties of conventional nylon-epoxy adhesives, a comparison of epoxy with other types of resin systems as reinforcing agents for nylon-base adhesives, a study of the relationship between the structure of nylon polymers and adhesion, and an investigation of various nylon polymers as fillers for epoxy adhesives.

Comparison of Epoxy With Other Resins as Reinforcing Agents for Nylon-Base Adhesives

The suitability of nylon-epoxy adhesive systems for use as structural adhesives at very low temperatures had been demonstrated previously (ref. 15), but the use of other types of resins as reinforcing agents appeared to offer a promising means of improving the properties of this type of adhesive that warranted research. In this program, selected phenolic, acrylic, ester, and urethane polymers were investigated as reinforcing agents for a variety of nylon-base adhesives (ref. 14, sec. VII).

TABLE VI.—*Comparison of Various Resin Systems as Reinforcing Agents for Nylon-Base Adhesives*

Code No.	Adhesive system ¹	Ratio	Tensile shear, psi ²		T-peel, ³ lb/in.	
			R.T.	−196° C	R.T.	−196° C
58	Nylon/epoxy	25/75	3910	2632	10.0	4.0
59	Nylon/epoxy	50/50	6110	2728	50.0	5.0
60	Nylon/epoxy	75/25	7455	3079	65.0	7.5
61	Nylon/phenolic ⁴	25/75	1195	1288	0	0.5
62	Nylon/phenolic ⁴	50/50	1820	1311	0	1.0
63	Nylon/phenolic ⁴	75/25	2708	1977	1.0	1.0
64	Nylon/acrylic	25/75	1526	1640	5.0	1.5
65	Nylon/acrylic	50/50	2210	3000	22.5	2.5
66	Nylon/acrylic	75/25	2555	1312	30.0	2.0
⁵ 67	Nylon/polyester	25/75	1662	780	0	0.5
⁵ 68	Nylon/polyester	50/50	1651	1066	0	0.5
⁵ 69	Nylon/polyester	75/25	1356	1034	5.0	2.0
70	Nylon/polyurethane	25/75	} Systems completely incompatible			
71	Nylon/polyurethane	50/50				
72	Nylon/polyurethane	75/25				

¹ Curing conditions were 1 hr at 177° C with 25 psi, except where noted.

² Average of 4 specimens.

³ Values for single specimens.

⁴ Cure staged from room temperature to 117° C in 20 min, 45 min at 117° C at 25 psi, staged from 117° C to 177° C, 1 hour at 177° C and 25 psi.

⁵ Systems partially incompatible.

The epoxy resin used in these experiments was made by adding 6 pts./100 resin (phr) of dicyandiamide to produce a resin with a gel time of 5 min at 177° C. Polyester and polyurethane were compounded with a nylon copolymer at three different levels of concentration. The tensile-shear and T-Peel strengths of bonds made with these experimental nylon adhesives are given in table VI. It is evident from the data that the epoxy resin was decidedly superior to the other three reinforcing resins evaluated.

Comparison of Different Nylons

Nylon polymers have proved to be useful adhesive compounds. These polymers are used as the prime adhesive component, as, for example, in the well-established nylon-epoxy blends; and, in finely powdered form, these polymers have proven useful as fillers in adhesive compositions. Because of the demonstrated effectiveness of nylon polymers in adhesives, the investigators carrying out this program undertook a comprehensive study of the effect of polymer composition on the performance of nylons in adhesives. Nylons with aliphatic

and with aromatic groups in the polymer chain were prepared as indicated in table VII by interfacial polymerization (ref. 14, sec. X).

Most of these experimental nylons were evaluated as fillers in epoxy-polyamide adhesives. Two of the experimental nylons that had low melting points (Code Nos. 18 and 48) were evaluated as resin components of adhesives. The polymers with softening points above about 140° C were not considered suitable as resin components of nylon-epoxy type adhesives because impractically high curing temperatures would be required to cause them to flow and fuse.

These experimental polymers differed considerably in their value as fillers in the epoxy-polyamide adhesive, but there was no discernible correlation between the structures of the nylons and their performances. It is also noteworthy that, despite the variety of experimental nylon polymers prepared and evaluated, none was superior to the commercial nylon copolymer in performance as a filler for the epoxy-polyamide adhesive.

Studies of experimental nylon polymers as components for nylon-epoxy type adhesives were undertaken to determine if the softening point of the nylon used had a significant effect on the performance of the adhesive. Experimental polymers, Code Nos. 18 and 48, (table VII), had softening points of 138° C and 30° C respectively, and, consequently, could be used in this type of adhesive. Two additional experimental polymers were prepared by heating a melt of two commercial polymers with the expectation of causing segment interchange. One of these polymers was prepared by heating a mixture containing 70 percent of Zytel 61 and 30 percent of nylon 11 (BCI-1107, Belding Corticelli Industries, Inc.) at 300° C for 2 hours; the other by heating similarly a mixture containing 75 percent of Zytel 31 (a nylon 6,10) and 25 percent of nylon 11. These four experimental polymers together with a sample nylon of type 8 were formulated into nylon-epoxy adhesives by conventional rubber milling and calendering techniques. Test specimens were prepared with bonding being accomplished by curing for 1 hour at 350° C under 25 psi pressure. The tensile-shear strength and T-Peel strength values are reported in table VIII. There was no apparent correlation between the softening point of the nylon polymer and the strength properties of the adhesive made from it, as far as can be ascertained from these results.

Exploratory Studies on Modified Nylons

Some exploratory work involving studies of modified nylon polymers also was undertaken (ref. 14, sec. X). Several novel ideas were explored, but it is difficult to assess the value of these ideas because, if the products developed in this exploratory work did not appear suitable for use at ambient temperature conditions, they were not

TABLE VII.—A Study of Nylon Polymer and Copolymer Chemical Structures to Optimize Adhesive Strength at Extremely Low Temperature
[Polymers and Copolymers Used as Fillers for Resin 3135]

Code No.	Nylon monomeric constituents	Softening point, °C	Adhesive compositions—Resin 3135 filled with 33.3 phr Nylon (200 mesh)		
			Tensile shear, ² psi		T-Peel, ³ lb/in.
			R.T.	−196° C	R.T. −196° C
1	Zytel 61 0.05 Mol Hexamethylene diamine.....	138 + 260(260)	3140	3180	2.0 2.5
			2263	2517	2.5 1.0
			2055	2242	2.5 1.5
2	0.05 Mol Hexamethylene diamine.....	+ 209(209)			
3	0.05 Mol Sebacyl chloride.....				
4	0.05 Mol Hexamethylene diamine.....				
5	0.05 Mol Oxaloyl chloride.....	320			
	0.05 Mol Ethylene diamine.....				
	0.05 Mol Adipoyl chloride.....		370	567	3.5 1.0
6	0.05 Mol Ethylene diamine.....	280			
	0.05 Mol Sebacyl chloride.....		1054	1137	3.5 0.5
	0.05 Mol Ethylene diamine.....				
36	0.05 Mol Oxaloyl chloride.....	>290 Decomposes			
	0.05 Mol Hexamethylene diamine.....				
	0.05 Mol Azelaoyl chloride.....		1444	1276	5.0 2.0
37	0.05 Mol Ethylene diamine.....	221			
	0.05 Mol Azelaoyl chloride.....		1295	1944	4.5 2.5
	0.05 Mol Hexamethylene diamine.....				
21	0.025 Mol Adipoyl chloride.....	+ 219(200)			
	0.025 Mol Sebacyl chloride.....		2112	1757	2.4 1.0

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30	0.05 Mol Ethylene diamine.....	226				
	0.025 Mol Adipoyl chloride.....					
	0.025 Mol Sebacyl chloride.....					
34	0.025 Mol Ethylene diamine.....	194	854	1114	5.0	1.5
	0.025 Mol Hexamethylene diamine.....					
	0.05 Mol Sebacyl chloride.....					
40	0.05 Mol Hexamethylene diamine.....	237				
	0.025 Mol Adipoyl chloride.....					
	0.025 Mol Azelaoyl chloride.....					
	0.05 Mol Hexamethylene diamine.....					
41	0.025 Mol Azelaoyl chloride.....	181				
	0.025 Mol Sebacyl chloride.....					
	0.025 Mol Ethylene diamine.....					
47	0.025 Mol Hexamethylene diamine.....	195	924	1132	7.5	2.0
	0.025 Mol Adipoyl chloride.....					
	0.025 Mol Sebacyl chloride.....					
49	0.10 Mol Ethylene diamine.....	152	998	1620	5.0	2.0
	0.10 Mol Hexamethylene diamine.....					
	0.10 Mol Azelaoyl chloride.....					
	0.10 Mol Sebacyl chloride.....					
Aromatic Nylons						
7	0.05 Mol Hexamethylene diamine.....	389	2128	2017	2.5	2.0
	0.05 Mol Terephthaloyl chloride.....					
8	0.05 Mol Hexamethylene diamine.....	165	2545	1166	(⁶)	2.5
	0.05 Mol Isophthaloyl chloride.....					

¹ Naranco Resin 3135 from Naranco Research and Development.² Cured approximately 48 hours at room temperature. Tested per MIL-A-5090D. Av. of 4 specimens.³ Cured approximately 48 hours at room temperature. Single specimen.⁴ Data from the literature.⁵ Failed in handling.

16	0.05 Mol Hexamethylene diamine.....	325	1209	1760	5.0	2.5
	0.025 Mol Sebacyl chloride.....					
	0.025 Mol Terephthaloyl chloride.....					
18	0.05 Mol Hexamethylene diamine.....	138	3085	1757	0	1.0
	0.025 Mol Adipoyl chloride.....					
	0.025 Mol Isophthaloyl chloride.....					
19	0.05 Mol Hexamethylene diamine.....	197	1328	744	7.5	1.5
	0.025 Mol Sebacyl chloride.....					
	0.025 Mol Isophthaloyl chloride.....					
28	0.05 Mol Ethylene diamine.....	257				
	0.025 Mol Sebacyl chloride.....					
	0.025 Mol Isophthaloyl chloride.....					
38	0.05 Mol Hexamethylene diamine.....	334	1626	1820	5.0	2.0
	0.025 Mol Azelaoyl chloride.....					
	0.025 Mol Terephthaloyl chloride.....					
39	0.05 Mol Hexamethylene diamine.....	204	2932	1457	3.5	2.5
	0.025 Mol Azelaoyl chloride.....					
	0.025 Mol Isophthaloyl chloride.....					
48	0.025 Mol Ethylene diamine.....	30				
	0.025 Mol Hexamethylene diamine.....					
	0.025 Mol Adipoyl chloride.....					
	0.025 Mol Isophthaloyl chloride.....					
50	0.10 Mol Ethylene diamine.....	369	782	1244	5.0	2.0
	0.10 Mol Hexamethylene diamine.....					
	0.10 Mol Azelaoyl chloride.....					
	0.10 Mol Terephthaloyl chloride.....					

¹ Narmco Resin 3135 from Narmco Research and Development.

² Cured approximately 48 hours at room temperature. Tested per MIL-A-5090D. Av. of 4 specimens.

³ Cured approximately 48 hours at room temperature. Single specimen.

⁴ Data from the literature.

⁵ Failed in handling.

TABLE VIII.—*Adhesive Strength of Nylon-Epoxy Adhesives Prepared With Experimental Nylons*

Nylon composition	Nylon softening point, ° C	Nylon-epoxy adhesive strength			
		Tensile shear, ¹ psi		T-Peel, ² lb/in.	
		R.T.	-196° C	R.T.	-196° C
Metlbond 406 (Control).....	138	5470+	4840	-----	8.33
0.5 Mol Hexamethylene diamine 0.025 Mol Adipoyl chloride..... 0.025 Mol Isophthaloyl chloride..	138	4812	2718	7.5	3.0
0.025 Mol Ethylene diamine..... 0.025 Mol Hexamethylene diamine..... 0.025 Mol Adipoyl chloride..... 0.025 Mol Isophthaloyl chloride..	30	5670	3285	10.0	5.0
Zytel 61 ³ 70%..... BCI-1107 30%.....	121	4390	3715	20.0	10.0
Zytel 31 ³ 75%..... BCI-1107 25%.....	162	4440	5022	6.0	10.0
Nylon-Type 8..... BCI-3218.....	⁴ 136	2112	1776	100.0	2.5

¹ Cure: 1 hr at 177° C and 25 psi. Av of 4 specimens.² Single specimens.³ Heated together above melting point to obtain segment interchange.⁴ Approximate.

evaluated further. A very brief discussion of some of this experimental work is presented here in the hope that it will stimulate further investigation because the ideas behind the exploratory work appear to have merit.

It was found, for example, that the Zytel 61 copolymer could be combined with butadiene diepoxide and resorcinol diglycidyl ether to produce modified nylon polymers that could be thermoset. Apparently the epoxide groups were grafted onto the nylon polymer chain. Similarly a low molecular weight aliphatic epoxy resin was apparently grafted onto the nylon polymer. These graft polymers were much higher in molecular weight than the nylon starting material and therefore were considered unsuitable for use at ambient temperatures. Accordingly, they were not evaluated sufficiently for appraisal of their utility.

Studies of Effects of Procedures for Making Nylon-Epoxy Blends

It is well known that the procedures employed to blend nylons and epoxy resins together to form adhesive compositions have an influence on the properties of the adhesive, probably because the nylon and epoxy will not form a homogeneous system. It is, however, of value to have available a direct comparison of various methods of combining the nylon and epoxy resins with all of the formulating and evaluation studies being carried out in one laboratory. Four methods of mixing were investigated by Narmco: (1) milling the nylon and epoxy together on a rubber mill at room temperature and then calendering an adhesive sheet from this mixture, (2) casting films from solutions of the two components, (3) converting the components to a gelled state by solvent action and then milling the materials together on a rubber mill (solvent milling), and (4) mixing the components together on a rubber mill hot enough to fuse them. Adhesives of identical composition were prepared by these four methods and evaluated by determining the tensile-shear strength of bonded 7075-T6 aluminum test specimens. The results are given in table IX (ref. 14, sec. VI). The adhesives prepared by solution mixing produced significantly stronger bonds than those prepared by other procedures.

TABLE IX.—*Effects on Tensile Shear Strength of Various Procedures for Preparing Nylon-Epoxy Adhesive Compositions*

Compounding process	Tensile shear, ¹ psi		
	² 127° C	³ R.T.	³ —196° C
Dry mixing and calendering (Standard Metlbond 406 Process)-----	420	4722	3450
Solution casting-----	531	5342	3512
Solution mixing and calendering-----	1602	6257	4057
Fused mixing and calendering-----	723	4806	2950

¹ Cured by staging from room temperature to 177° C in 20 min and holding 1 hr at 177° C and 25 psi.

² Av for 4 specimens.

³ Av for 8 specimens.

Investigation of Fillers for Epoxy-Polyamide Adhesives

It is common practice to incorporate fillers into adhesives to improve their properties. Fillers are particularly useful for controlling the flow properties of an adhesive and they frequently contribute to

strength. It is generally agreed desirable to have the coefficient of thermal expansion of an adhesive approximately the same as that of the adherend to minimize the stresses that result from expansion and contraction caused by temperature changes. However, fillers also have effects on properties other than the coefficient of expansion and the best filler is not necessarily the one that reduces the coefficient of expansion of the adhesive to near that of the metal. The effects of fillers on the strength properties and the thermal expansion of epoxy-polyamide adhesives were studied with interesting results in the Narmco program (ref. 14, sec. XI).

Four fillers with widely different coefficients of thermal expansion were selected for investigation. Zytel 61 nylon has a coefficient of expansion greater than that of the 7074-T5 aluminum used for making test specimens, powdered aluminum has about the same coefficient, and silica and alumina have coefficients lower than that of the metal alone. Adhesives were compounded with 33.3, 67.7, and 100 parts of filler per 100 parts of epoxy-polyamide resin. In compounding the filled adhesives, half of the filler was dispersed in the epoxy resin and half in the polyamide curing agent before they were mixed. Tensile-shear test specimens were prepared with 7074-T5 aluminum. The data obtained together with the coefficients of thermal expansion of the adhesives are shown in table X. The values given for the coefficients of expansion are average values for the temperature range -196°C to 0°C .

The adhesive containing powdered nylon as a filler was generally superior to the others in tensile-shear strength at -196°C and at the 33.3 phr filler level was decidedly superior to the others. There was no apparent correlation between the strength of the adhesive and its coefficient of expansion.

DEVELOPMENT OF ADHESIVE-BONDED STUDS

A striking demonstration of the capabilities of structural adhesives was an important contribution of work done for the George C. Marshall Space Flight Center under Contract NAS 8-5188 by Narmco Research and Development Division of Whittaker Corp. (ref. 16). The objective was to develop a satisfactory means for attaching aluminum studs to an aluminum structure with an adhesive that would cure at room temperature. The design of the studs is shown in figure 3.

A novel accomplishment of this program was the discovery that the inclusion of a thin sheet of elastomeric material in the glue line would improve the resistance of adhesive bonds to shock and impact. A reasonable explanation appears to be that the elastomeric film acts to absorb shock and to distribute stresses within the glue line. Using

TABLE X.—*Study of Fillers for Epoxy-Polyamide Adhesive Bonding at Extremely Low Temperatures*

Filler, pts. by weight/100 pts. Narmco Resin 3135	Coefficient of linear thermal expansion (-320 to +32° F) in./ in./°F × 10 ⁶	Tensile-shear strength, ¹ psi	
		R.T.	-320° F, -196° C
Unfilled control.....	3. 21	2682	1514
Nylon (<200 mesh):			
33.3.....	3. 17	3140	3180
66.7.....	3. 15	2150	2895
100.0.....	3. 18	1970	2307
Aluminum (18 micron average):			
33.3.....	2. 72	3400	1877
66.7.....	2. 50	3230	2672
100.0.....	2. 21	2610	2960
Silicon dioxide (quartz, <200 mesh):			
33.3.....	2. 69	2530	1570
66.7.....	2. 10	2720	1782
100.0.....	1. 87	2480	2130
Alumina (<200 mesh):			
33.3.....	2. 44	2900	1935
66.7.....	2. 23	2650	1982
100.0.....	1. 88	2830	1935

NOTE.—Curing cycle, 48 hr. at R.T. and contact pressure.

¹ Av. of 8 specimens each.

this concept, the investigators succeeded in bonding aluminum studs to aluminum structures so securely that failures under stress occurred in the metal and not in the bond.

The optimum adhesive system developed in this program consisted of an adhesive and a thermoplastic polyurethane film 1-5 mils thick. The adhesive is a polyurethane-modified epoxy that cures at room temperature.

The technique used for making the bonds was found to be of critical importance, as is frequently the case in adhesive bonding operations. It was found essential to degrease thoroughly the aluminum surfaces to be bonded; to etch them in a sodium dichromate-sulfuric acid etching bath; and to degas the adhesive under a vacuum before use, since any gas bubbles in the glue line cause a pronounced lowering of bond strength.

The use of an elastomeric film in a glue line for stress distribution is a simple, practical technique that should be useful in the manufacture of many widely diversified commercial products. It is, of course, necessary that a good adhesive bond be obtained at all of the surfaces in contact with the adhesive.

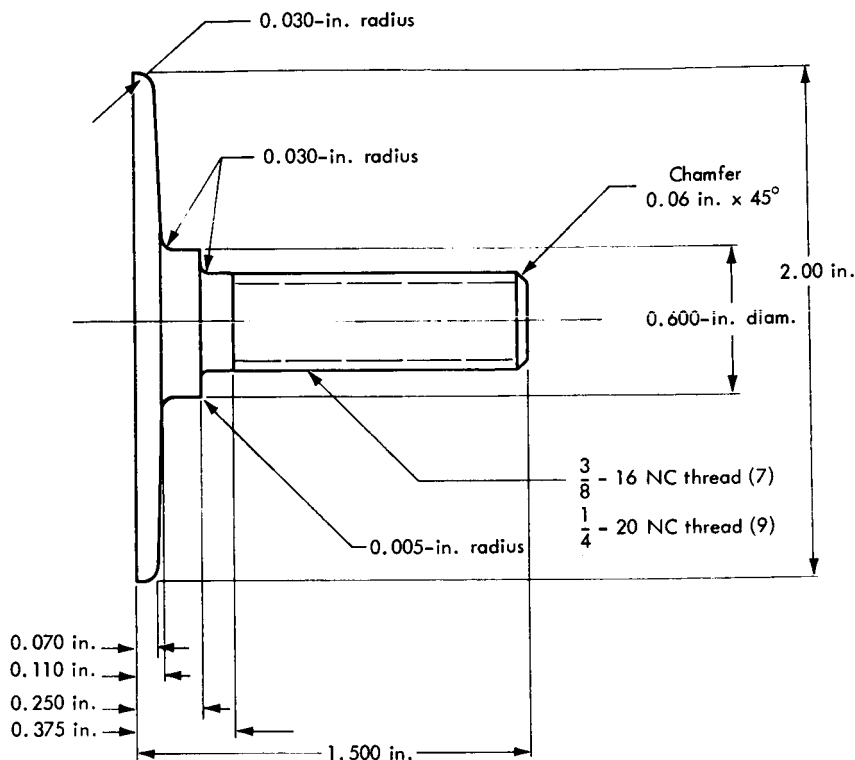


FIGURE 3.—Design of stud for adhesive bonding.

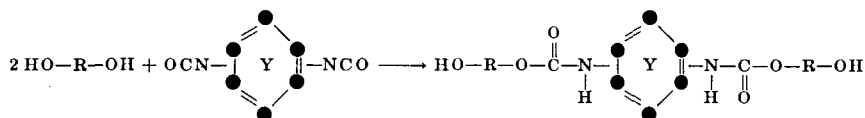
DEVELOPMENT OF IMPROVED ADHESIVES

The Marshall Space Flight Center of NASA sponsored an interesting research program on adhesives at the Central Research Laboratories of the Borden Chemical Co. under Contract NAS 8-11518 (refs. 17, 18, 19, 20, 21, and 22). This program was concerned with the development of adhesives that would perform satisfactorily over a temperature range of -253°C to 205°C . A wide variety of unusual polymers was synthesized and evaluated, providing suggestions and incentives for further investigation of these materials for development into commercial products. It was necessary in an exploratory research program of the type carried out by Borden to restrict the evaluation of the products to the minimum required to identify potentially useful materials. A more detailed evaluation, of course, might disclose deficiencies. The principal contribution of the Borden program was the development of potentially useful new types of polymers. No attempt was made to develop finished adhesives.

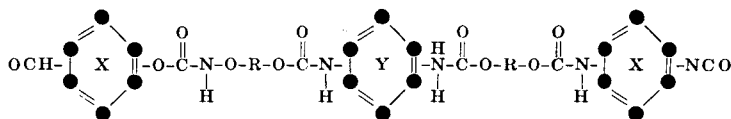
The following classes of polymers were studied: polyisocyanates, epoxies, epoxy esters, poly-2-oxazolidones, polyimides, and polyisocyanurates. The research in each area is discussed separately below. These discussions are restricted in scope to the significant contributions of the program to adhesive technology. The details of the syntheses of the various compounds prepared are not discussed here; they may be found in the references cited.

Polyurethanes

Polyurethane adhesives are of particular interest because of their demonstrated good performance at low temperatures (ref. 23). Although polyurethane adhesives can be made with a wide range of properties, only the flexible or elastomeric types are of interest for use at very low temperatures (ref. 24). The flexible polyurethanes are commonly made by combining a moderately high molecular weight glycol with an aromatic diisocyanate to form a hydroxyl-terminated prepolymer as illustrated (ref. 25):



This hydroxyl-terminated prepolymer is then combined with a diisocyanate (generally different from that used to prepare the hydroxyl-terminated prepolymer) to form an isocyanate-terminated prepolymer which may be represented as



These prepolymers are then combined with a diol or diamine coupling agent to produce high molecular weight polymers. The properties of polymers of this type have been exhaustively investigated, with principal interest being centered on their performance as elastomers (ref. 26). Published studies of these polymers as adhesives are less extensive (ref. 27).

The investigators at Borden prepared a large number of urethane polymers and evaluated them as adhesives. The two composition variables studied most thoroughly were the glycol component incorporated in the hydroxyl-terminated prepolymer and the coupling agents used to convert the isocyanate-terminated prepolymers into the desired high molecular weight product.

Two types of glycols were investigated—polyether glycols and polyesters (hydroxyl terminated). The polyurethane adhesives prepared with the polyether glycols were judged to be consistently better than those prepared with the polyesters. The evaluation of these experimental adhesives was limited to determinations of tensile-shear strength of lap joints of aluminum at -196°C , 21°C , and 121°C . The superiority of the polyether glycol-base polyurethane adhesives was most evident in the tests made at -196°C .

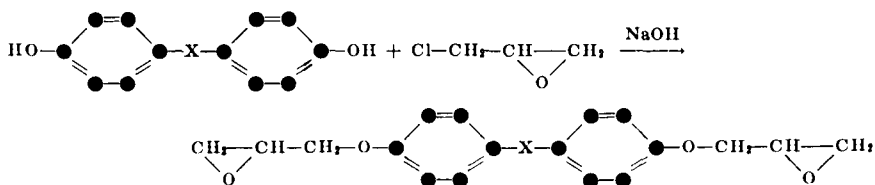
The coupling agents investigated included aromatic diamines, polyether glycols, aliphatic glycols, and polyesters. The aromatic diamines, especially MOCA (3,3'-dichloro-4,4'-diamino-diphenyl-methane), were judged to be the best coupling agents.

An adhesive prepared from a commercially available isocyanate-terminated prepolymer, Adiprene L-315, was found to be superior to any of the experimental polyurethane adhesives prepared in the program. An adhesive prepared with Adiprene L-315 and MOCA had tensile-shear strengths of 6430 psi, 4580 psi, and 1365 psi at -196°C , 21°C , and 121°C , respectively. None of the experimental products equals this performance, although a few had adhesive properties almost as good as these.

Epoxy Resins

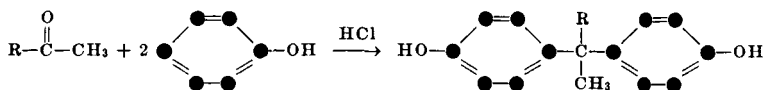
Epoxy adhesives of various types have been used extensively in NASA programs and have proven satisfactory for many types of service (refs. 28 and 29). However, no epoxy adhesives were known that were entirely satisfactory for use at very low temperatures (refs. 30 and 31). A study of epoxy resins of the bisphenol type and of epoxy esters was made in the Borden program in an effort to develop adhesives that would provide satisfactory service over a wide range of temperatures, from cryogenic to 205°C .

Bisphenol-type epoxy adhesives.—Epoxy resins of the type derived from the reaction between bisphenol and epichlorohydrin were studied in attempts to develop adhesives of improved performance at cryogenic temperatures (ref. 17). The reaction sequence is represented by the following:

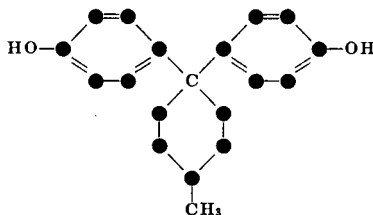


The bridge groups (X) were SO_2 , $\text{C}(\text{CF}_2\text{Cl})_2$ and $\text{C}(\text{R})\text{CH}_3$, in which

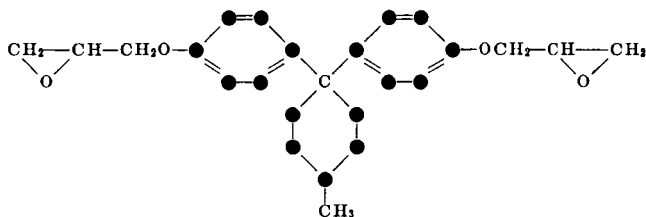
R was C_9H_{19} , $C_{15}H_{31}$, C_7H_{15} , and $(CH_2)_2CO_2H$. The compounds were synthesized by the reaction of 1 mole of ketone with 2 moles of a phenol with hydrogen chloride as catalyst, as illustrated below:



The most interesting experimental adhesive prepared in this phase of the program was derived from a bisphenol produced by the reaction of methyl cyclohexanone with phenol. This reaction product is illustrated below:



This bisphenol was combined with epichlorohydrin to produce the following monomer:



An adhesive was prepared from this material by mixing it with 4,4'-diaminodiphenylmethane. Lap-joint test specimens of aluminum and stainless steel were bonded with this adhesive and the tensile shear strengths of the bonds were determined. Test results are shown in table XI. This adhesive was considered to have the best performance over a wide range of temperature conditions of any of the epoxy resins evaluated; including several commercial products.

A large number of experimental epoxy resins were prepared by the synthesis method described above. In each instance, the bisphenol

TABLE XI.—*Tensile-Shear Strength of Experimental Epoxy Adhesive*

Temperature, ° C	Tensile-shear strength, psi	
	on aluminum	on stainless steel
—196.....	4800	3870
20.....	3490	2350
121.....	2079	2095

was converted to an epoxide by combination with epichlorohydrin and the resulting epoxide was cured with 4,4'-diaminodiphenylmethane. Thus, a series of adhesives was prepared in which the epoxy resins differed only in the structure of the bisphenol. Table XII shows the various bisphenols that were used together with the tensile-shear strengths of adhesive bonds made with epoxy adhesives based on these bisphenols. The epoxy content was shown to be the predominant factor in determining the strength of the experimental resins derived from the various bisphenols regardless of the polarity of the substituents on the aromatic ring or alkyl groups. However, variations in the adhesive performance of some of the resins showed that steric factors also contributed to adhesive strength. Substituents in the 3,3',5,5' positions of the benzene rings in the bisphenol were found to be detrimental to adhesive strength, probably because of reduced adhesion between the epoxy resin and the metal adherend. For example, the adhesive strength of the epoxy resin derived from 2,2-bis(4,4-dihydroxy-3,3'-diethyl-5,5'ditertiarybutyl)propane was zero at all temperatures. Lesser effects were observed when the substituents were methyl, bromine, or chlorine. None of the structural modifications was effective in increasing the flexibility and the adhesive strength at -196°C .

The epoxy resin derived from 4,4'-dihydroxybiphenyl and epichlorohydrin (ref. 18) was evaluated with the expectation that the more rigid biphenyl structure would increase the high-temperature shear-tensile strength. Since the resin was a high melting solid and could not be properly mixed with a diamine for curing at low temperatures, it was evaluated in mixtures with a liquid epoxy resin derived from bisphenol A and cured with 4,4'-diaminodiphenylmethane. The tensile strengths of lap-joint seals on aluminum measured at 121°C were in the range of 2200–3300 psi. Although the properties were attractive, the adhesive was not considered further because a temperature of 165°C was required to melt and cure the resin.

TABLE XII.—*Tensile-Shear Strength of Bond Prepared with Experimental Epoxy Adhesives*

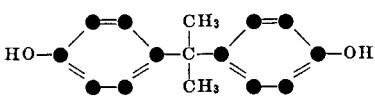
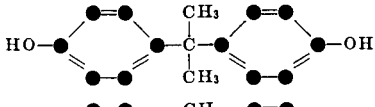
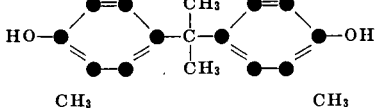
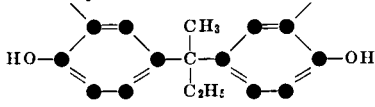
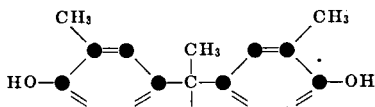
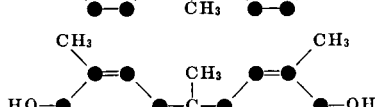
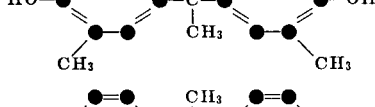
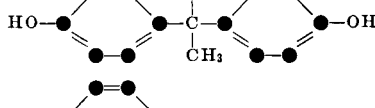
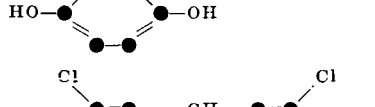
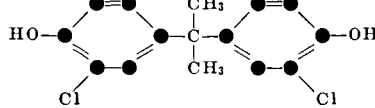
Structure of bisphenol ¹	Epoxy con- tent	Tensile shear strength, psi at various temperatures (°C)					
		On aluminum			On stainless steel		
		-196	20	121	-196	20	121
	0.542	3630	2170	1754	4300	2850	2052
	0.531	4200	2610	1804	4070	2690	1931
	0.500	4270	2310	1685	3160	2420	1258
	0.428	3670	-----	-----	1528	2090	112
	0.485	3570	1478	351	3000	1757	1549
	0.362	2120	-----	-----	-----	-----	-----
	0.505	3180	-----	-----	-----	-----	-----
	0.668	2030	1890	75	-----	-----	-----
	0.302	680	1391	557	864	1005	~0
	0.162	~0	~0	~0	~0	~0	~0

TABLE XII.—*Tensile-Shear Strength of Bond Prepared with Experimental Epoxy Adhesives—Continued*

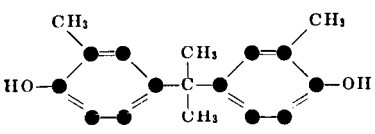
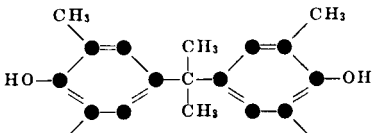
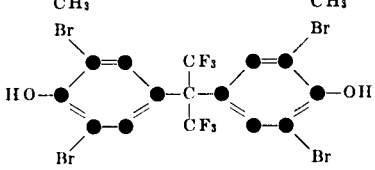
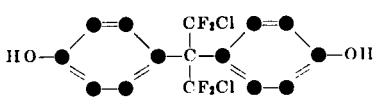
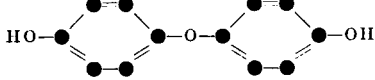
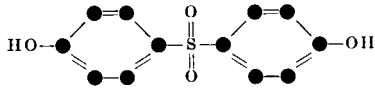
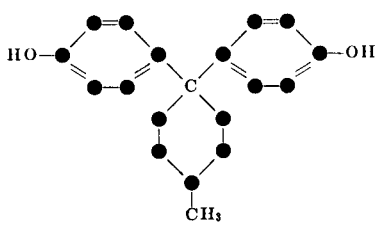
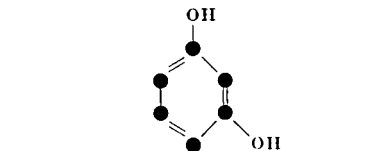
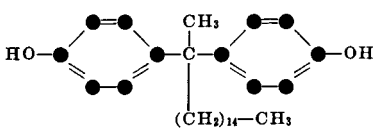
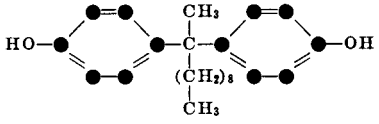
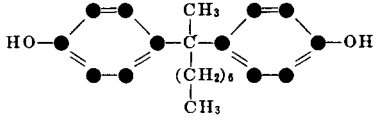
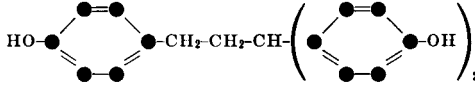
Structure of bisphenol ¹	Epoxy con- tent	Tensile shear strength, psi at various temperatures (°C)					
		On aluminum			On stainless steel		
		-196	20	121	-196	20	121
	0.419	3510	2890	850	2200	1800	1660
	0.40	2680	2240	943	462	645	227
	0.235	1143	1130	1799	1325	1577	1605
	0.336	1950	1867	959	3120	2580	352
	0.532	3910	1763	564			
	0.341						
	0.452	4800	3490	2079	3870	2350	2095
	0.668	3660	3450	364	3140	2760	213

TABLE XII.—*Tensile-Shear Strength of Bond Prepared with Experimental Epoxy Adhesives—Concluded*

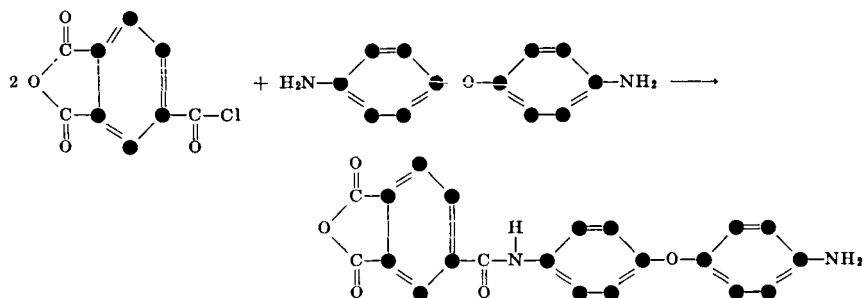
Structure of bisphenol ¹	Epoxy content	Tensile shear strength, psi at various temperatures (°C)					
		On aluminum			On stainless steel		
		-196	20	121	-196	20	121
	0.20	0	132				
	0.36						
	0.335						
	0.438						

¹ Adhesives prepared by combining bisphenol with epichlorohydrin to form diepoxide and curing with equivalent amount of 4,4'-diaminophenylmethane.

Epoxy Curing Agents

Another technique examined in the Borden studies for improving high-temperature strength was the use of high melting compounds that contained amide linkages and anhydride groups or amine groups, or both anhydrides and amines, to react with the epoxide.

A new curing agent was synthesized from trimesic acid anhydride chloride and 4,4'-diaminodiphenyl ether according to the reactions:

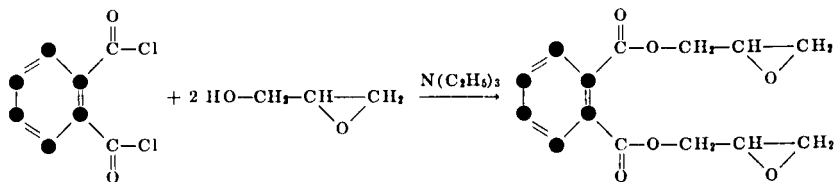


An adhesive prepared by curing Dow epoxy resin 332 with a mixture of the above compound and 4,4'-diaminodiphenylmethane had a shear-tensile strength of 2510 psi at 121° C, which was higher than the strength of the same resin cured with the 4,4'-diaminodiphenylmethane alone.

Additional studies demonstrated that the tensile-shear strength of resins cured with cyclopentanetetracarboxylic acid dianhydride was above 1300 psi when tested at 205° C.

Epoxy Esters

A major part of Borden's investigation of epoxy adhesives was devoted to a study of epoxy esters, and several interesting adhesives were developed. The general method used to prepare these esters involved the reaction between an acid chloride and glycidol in the presence of a tertiary amine. This reaction is illustrated by the following example for the reaction of phthaloyl chloride and glycidol:



To obtain a satisfactory product, it was found necessary to add the acid chloride and the tertiary amine separately and simultaneously in equivalent amounts to the cold glycidol.

The glycidol esters of phthalic acid, isophthalic acid, terephthalic acid, trimesic acid, hexahydroterephthalic acid, and pyromellitic acid were prepared. These epoxy esters were cured with 4,4'-methylenedianiline (MDA) or cyclopentanetetracarboxylic acid dianhydride to form adhesives. The tensile-shear strengths of bonds of lap-joint aluminum test specimens bonded with these experimental adhesives are shown in table XIII. These data show that epoxy adhesives of this type can be made that will give good strength at low temperatures (-196° C) or at high temperatures (205° C), but none of these adhesives had good tensile-shear strength at both low and high temperatures.

Poly-2-oxazolidones

Many polyurethanes have good adhesive properties at low temperatures but fail at high temperatures, whereas epoxy resins have good adhesive properties at high temperatures but are not satisfactory at low temperatures. Borden investigated the feasibility

TABLE XIII.—*Tensile-Shear Strength of Bonds Prepared With Epoxy Ester Adhesives*

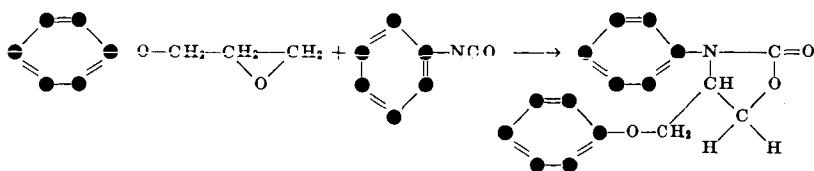
Sample No.	Description of ester	Curing agent	Tensile shear strength			
			-196° C	20° C	121° C	205° C
471-21----	Diglycidyl isophthalate----	MDA	4200	3780	2660	385
462-59-6---	Diglycidyl isophthalate----	MDA	4100	2900	-----	312
461-89-----	Diglycidyl phthalate-----	MDA	-----	2870	944	-----
461-128----	Diglycidyl hexahydro- terephthalate.	MDA	3390	-----	-----	282
467-113----	2,2'-Diglycidyl diphenolate.	MDA	3660	3720	-----	216
461-126-1--	Triglycidyl trimesoate----	MDA	2010	-----	-----	1040
471-24-----	Diglycidyl terephthalate--	CPTCA	1440	1890	2050	899
461-91-----	Triglycidyl trimellitate----	CPTCA	901	1920	1970	1040
461-93-----	Triglycidyl trimesoate----	CPTCA	1270	1830	1810	1100
461-95-----	Tetraglycidyl pyro- mellitate.	CPTCA	-----	507	-----	-----
461-111----	Tetraglycidyl pyro- mellitate.	CPTCA	2930	-----	-----	1120
461-114----	Tetraglycidyl pyro- mellitate.	CPTCA	1580	-----	-----	1190

MDA=4,4'-methylenedianiline.

CPTCA=cyclopentanetetracarboxylic acid dianhydride.

of achieving a combination of the good high-temperature adhesive properties of the epoxy resins and the good low-temperature adhesive properties of the polyurethanes by preparing adhesives from the products of reactions between epoxy resins and isocyanate-terminated urethanes.

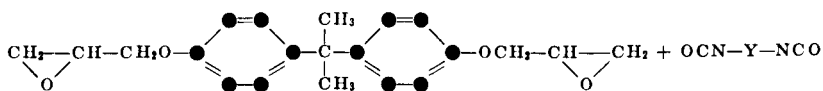
The reaction between an epoxide and an isocyanate to form a 2-oxazolidone is illustrated by the following reaction between phenylglycidyl ether and phenyl isocyanate to form 3-phenyl-5-methyl-2-oxazolidone:



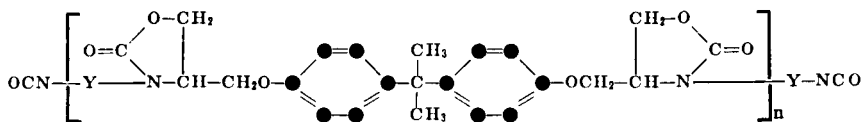
3 phenyl-4-phenoxyethyl-2-oxazolidone

The reaction between an epoxy resin derived from bisphenol A and

an isocyanate-capped urethane was expected to follow the same route:



would yield

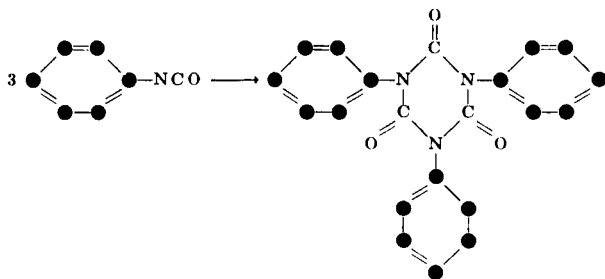


The oxazolidone rings combined with the bisphenol A segments were expected to increase the rigidity of the polymer and increase the strength at higher temperatures. The polymer adhesive was expected to remain flexible at low temperatures because of the presence of the urethane segments.

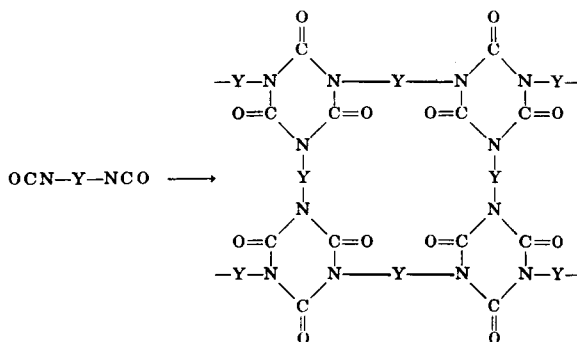
Borden prepared polymers of this type by the reaction of epoxy resins with a polyether glycol that was end-capped with isocyanate groups. The adhesive that had the best performance over a broad temperature range was made from a glycidyl ether (derived from bisphenol A), an isocyanate-capped polytetramethylene ether glycol, and 4,4'-diaminodiphenylmethane in the ratio 5:2:1.8. The shear-tensile strengths were 3640, 3750, and 2580 psi at -196°C , 20°C , and 121°C , respectively.

Polyisocyanurates

The trimerization reaction of isocyanate groups was investigated as a means for preparing polymers that had good adhesive properties over a broad temperature range. The trimerization reaction is illustrated by the formation of triphenyl isocyanurate from phenylisocyanate:



A similar reaction of a diisocyanate or an isocyanate-terminated polymer was expected to form a highly cross-linked polymer with a structure such as the following:



Adhesives derived from polymers of this type were expected to have improved strength at high temperatures, and when an isocyanate-terminated polyglycol ether was polymerized it was expected to maintain adhesive strength at low temperatures also.

TABLE XIV.—*Tensile-Shear Strength of Bonds Prepared with Polyisocyanurate Adhesives*

Description	Tensile-shear strength, psi, on aluminum			
	-196° C	20° C	121° C	205° C
Diphenylmethane diisocyanate (ref. 19) ..	1260	1165	1510	804
Copolymer of diphenylmethane diisocyanate and isocyanate-capped polyglycol prepolymer (1.5/1.5 reaction ratio) (ref. 20) ..	2490	1132	885	794
Copolymer of diphenylmethane diisocyanate and isocyanate-capped polyurethane prepolymer (1.5/1.5 reaction ratio) (ref. 21) ..	1630	1530	1410	1410
Copolymer of diphenylmethane diisocyanate and isocyanate-capped polyurethane prepolymer (1.5/1.5 reaction ratio) (ref. 22) ..	2280	1990	1150	1100
Copolymer of diphenylmethane diisocyanate and isocyanate-capped polyurethane prepolymer (1.5/1.5 reaction ratio) (ref. 22) ..	1960	1760	1460	1200

NOTE.—The compositions of the prepolymers were not disclosed. None of these experimental adhesives had outstanding properties. Nevertheless, the results are encouraging because some of these adhesives showed little loss in strength as the testing temperature was raised to 200° C. Further exploration of this approach to developing adhesives appears desirable.

The tensile-shear strengths of adhesives derived from diphenylmethane diisocyanate and copolymers of diphenylmethane diisocyanate are given in table XIV.

Elastomeric Sealants

The aerospace programs of NASA require sealants that perform satisfactorily at relatively high temperatures (up to 300°C) for extended periods of time and also sealants that perform satisfactorily at extremely low temperatures (as low as -250°C). This survey did not disclose any research that had been or was being done by NASA in the field of elastomeric sealants for high-temperature service. This lack of research by NASA would indicate that most of its requirements for such materials have been satisfied by the materials already developed by industry (refs. 48, 49, 50, and 51). The manufacturers of silicone polymers have, through their own research efforts, developed the technology of these materials to an advanced state.

Also, this survey does not include the somewhat related fields of potting and encapsulating compounds where NASA has made important contributions to technology. However, reports on NASA-sponsored research on potting and encapsulating compounds were reviewed in an effort to locate any technology that could be directly transferable to sealants.

NASA's requirements for sealants for service at very low temperatures are more specialized, and NASA has sponsored a major research program on the development of elastomeric sealants for use at very low temperatures. This research is of particular interest because the development of an elastomeric seal material for service at temperatures as low as -250°C presents many technical problems. Prior to application the sealant must be a mastic composition having sufficient fluidity to flow into the cracks and crevices that are to be sealed, and, after application, the sealant composition must cure (preferably at normal temperatures) into an elastomeric compound having good adhesion to the substrate. The cured sealant must withstand the strains and stresses imposed as the temperature of the sealed article varies over wide ranges without cracking or pulling away from the substrate. Ideally, the polymer in a sealant for this use should be elastic at the temperature of liquid hydrogen (-253°C), but no known elastomeric polymer satisfies this requirement. Even

those polymers best suited for low-temperature service cease to be elastomers at temperatures well above -250°C . Practically, then, the development of a sealant for use at temperatures near -250°C requires that a means be found to minimize the importance of true elasticity in the polymer. A technique that shows promise for accomplishing this has been developed in a research program of the Marshall Space Flight Center carried out by Hughes Aircraft Company under Contract NAS 8-2428 (refs. 52, 53, and 54). The principle involved in minimizing the importance of the elasticity of the polymer is to mix with the polymer a filler, such as glass fiber, that has a very low coefficient of thermal expansion to make a sealant with approximately the same coefficient of thermal expansion as the substrate to which it is to be applied. This principle should be useful in the development of commercial sealants for a variety of services.

The work by Hughes Aircraft Co. also included the evaluation of proprietary sealant materials and the synthesis of new polymers for sealants. Although the development of new polymers had not reached the stage of successful use of the new polymers in sealants at the time of the latest report available to this survey (ref. 54), the information obtained on methods of synthesis and the properties of the new polymers should be of great interest and value to others who are concerned with polymer research and development.

A somewhat detailed review of the results reported on the work done under Contract NAS 8-2428 is presented here to show the scope of the work and to indicate the more potentially fruitful lines for future research.

SEALANTS MADE FROM COMMERCIAL POLYMERS

The initial phase of the Hughes Aircraft research program involved a study of the validity of certain basic concepts of sealant design. Commercially available polymers were used in this study. It was assumed that the most suitable polymers would be those having low glass-transition temperatures and minimum tendencies to crystallize at low temperatures. It was further postulated that the need for elasticity at low temperatures could be minimized by compounding the sealants with fillers to make the coefficient of thermal expansion of the sealant about the same as that of the substrate. If this condition could be satisfied, the sealant would be subjected to little strain as the result of temperature changes.

Screening Evaluation of Commercial Polymers

Preliminary screening evaluations were made of 35 commercially available polymers to compare their flexibilities at the temperature

of liquid nitrogen (-196°C). The chemical compositions of the commercial polymers were not known and they could be characterized only by general class. Most of the commercial polymers were identified as either silicone-base or polyurethane-base polymers, but several polysulfides, epoxy-base polymers, and proprietary materials of unidentified classes were included among the 35 polymers. Coatings of these commercial polymers (approximately $\frac{1}{8}$ in. thick) were applied to aluminum panels and cured. The panels were then placed in an apparatus for evaluating flexibility that conformed to the design shown in MIL-8-8516; they were cooled to liquid nitrogen temperature, and bent to a 2-in. radius. All of the 35 polymers cracked in this bending test, but there were pronounced differences in the extent and type of damage that occurred, and it was possible to differentiate among the performances of some of the polymers. Two of the commercial polymers, one a polyurethane and the other a silicone, were judged on the basis of these low-temperature flexibility tests to be

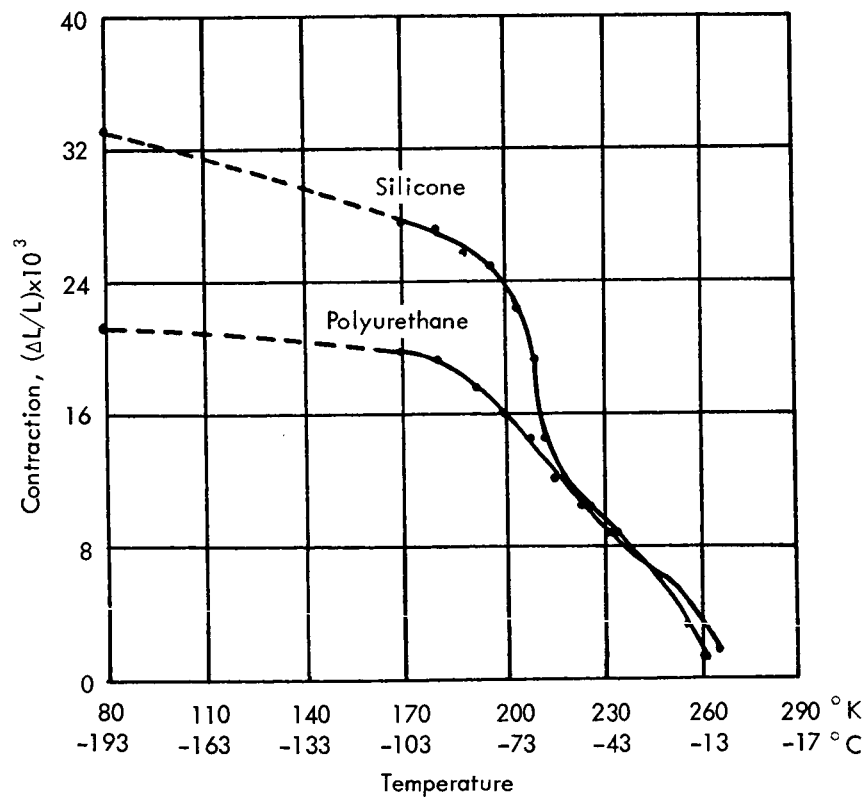


FIGURE 4.—Contraction of experimental sealants on cooling (ref. 52).

more suitable than the others for use as elastomeric sealants for low-temperature service. The polyurethane was Adiprene L100 (ref. 52) cured with castor oil, and the silicone was identified only as 3M Company's EC 1667, a proprietary material.

These two polymers were evaluated further by determining how much they contracted when cooled to low temperatures (ref. 52). Blocks of the polymers were cast and cured, and the changes in the lengths of the blocks were determined as the temperature was lowered in approximately 15° C increments from about -10° C to about -100° C and then in one increment to -193° C. Figure 4 shows the pronounced difference in the contraction of the two polymers. The silicone polymer underwent a distinct transition at about 60° C, as evidenced by the inflection in Curve A (refs. 55 and 56). The polyurethane polymer (Curve B) did not show an identifiable transition under the conditions of the experiments.

The contraction characteristics of the polyurethane would be more desirable than those of the silicone, since the great contraction of the silicone between -60° C and -70° C would produce high stresses in the silicone sealant when the temperature of a joint sealed with this material passed through this range. These findings led to the selection of the polyurethane Adiprene L100, cured with castor oil, as the most suitable of the commercial polymers evaluated for use in sealant compounding studies.

PREPARATION AND EVALUATION OF SEALANTS MADE FROM THE SELECTED POLYURETHANE

As indicated earlier, one objective of the program carried out under Contract NAS 8-2428 was to investigate the possibility of developing mixtures of fillers and polymer that would perform better as low-temperature sealants than the polymer alone. A few preliminary experiments demonstrated that this approach might be feasible.

A $\frac{1}{8}$ -inch thick composite of six layers of 181-type glass fabric and the polyurethane did not crack or show other evidence of failure when bent to a 2-inch radius at -196° C, whereas the polymer alone cracked under similar conditions. Figure 5 shows the relative contraction of the polyurethane alone and of a mixture of the polyurethane and E-glass fibers. The average coefficient of thermal contraction for the glass-filled polyurethane was 29×10^{-6} in./in./°K (approximately that of aluminum) compared to 85×10^{-6} in./in./°K for the unfilled polyurethane.

The results of these preliminary experiments were encouraging,

and the general feasibility of the concept was demonstrated by sealing simulated sections of a LOX tank with a glass-fiber-reinforced polyurethane and subjecting the sealed joints to repeated exposure to liquid nitrogen. The sealant flowed into the crevices fairly well, it cured under heat lamps, and it withstood the repeated exposure to liquid nitrogen. These results appeared to confirm the concept on which this phase of the program was based and indicated that the prospects for developing a satisfactory sealant based on the polyurethane were promising enough to justify further effort.

Two sealant compositions based on the polyurethane made by curing Adiprene L100 with castor oil were developed to the stage where specifications for the compositions were prepared and submitted to NASA (ref. 54). One of these sealant compositions was a foamed-in-place type that offered the advantage of low density; the other was a solid. The components and methods of compounding and application are described as follows.

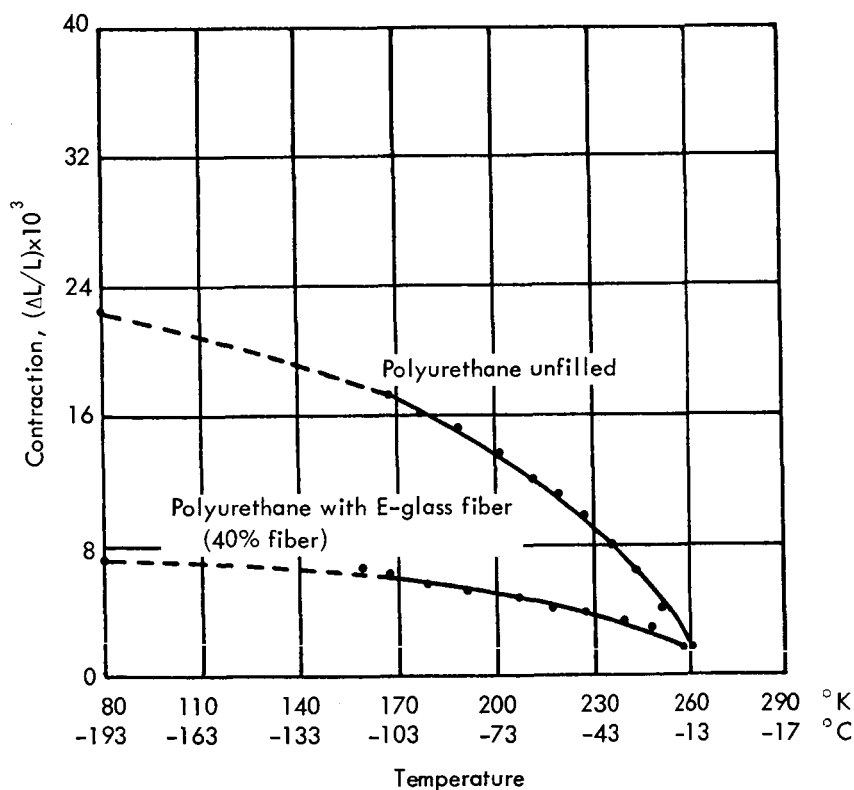


FIGURE 5.—Contraction of glass-fiber filled and unfilled polyurethanes on cooling (ref. 52).

Foamed-In-Place Sealant

Composition		
Component	Material	Pts by wt
A-----	{ Adiprene L100-----	100. 0
	{ Fiberfax washed fibers-----	42. 6
		142. 6
B-----	{ Castor oil, U.S.P.-----	24. 8
	{ SF1066 Surfactant-----	2. 0
	{ Benzyldimethylamine-----	1. 5
	{ Water (distilled)-----	0. 6
		28. 9

Mixing Procedures

Component A.—The Fiberfax fibers were dried at 100–110° C for at least 1 hour, cooled to room temperature, and then mixed with the Adiprene L100 in a Hobart mixer, or equivalent, until a uniform blend was obtained.

Component B.—The castor oil was placed in a mixer that provided good agitation, and the other components were added in the order listed above.

Sealant.—Component A was added to Component B in a heavy-duty mixer. It was recommended that no more be prepared than would be used in about 30 minutes.

Application

This sealant was designed for use on aluminum substrates, and its performance on other substrates was not evaluated. The recommendations for use were as follows:

The surfaces to be sealed must be thoroughly cleaned with acetone or methyl ethyl ketone; then apply one brush-coat of Chemlock¹ 607 primer to the cleaned surfaces and allow it to air dry not less than 30 minutes before application of the sealant. The sealant mixture can be applied with a caulking gun or with a trowel. The sealant will cure to a tack-free condition in 8 hours at 25° C and is fully cured in 18 hours at this temperature, but a 4-hour post-cure at 65° C substantially improves its properties.

Properties of Cured Foamed Sealant

The expected density of the fully cured foamed sealant prepared and applied as described above is 20 ± 2 lb/ft³ (determined by the method of ASTM–D–1622), and the expected peel strength is 5 lb/in. minimum, at room temperature and 1 lb/in. minimum at –196° C

¹ Hughson Chemical Co., Erie, Pa.

(determined by the method of ASTM-D-1876). The results from evaluations of several laboratory-prepared sealants indicated that much higher peel strengths were obtainable, and, since the failures in the peel test were predominantly adhesion failures, it is probable that improvements in surface preparation and in priming would result in higher minimum peel strengths. The cured sealants on aluminum panels were shown to withstand a thermal shock test consisting of five cycles of immersion in liquid nitrogen and warming to room temperature with no visible signs of deterioration.

Solid Sealant

Composition

<i>Material</i>	<i>Pts by wt</i>
Adiprene L100.....	100
Milled glass fibers ¹	30
Castor oil, U.S.P.....	24

¹ Milled glass fibers, $\frac{1}{32}$ - $\frac{1}{4}$ in. long obtained from Owens-Corning Fiberglas, Los Angeles, Calif.

Mixing Procedure

The glass fibers were dried at 100-110° C for at least 1 hour and then thoroughly mixed into the Adiprene L100 in a Hobart mixer, or equivalent. Immediately prior to use, the castor oil was added, and the components were mixed until a uniform blend was obtained.

Application

This sealant was designed for use on aluminum substrates. The recommendations for use were as follows:

The surface of the aluminum must be cleaned by washing with acetone or methyl ethyl ketone; then apply one brush-coat of Chemlock 607 to the cleaned surfaces and allow to air dry for at least 30 minutes before applying the sealant. The sealant mixture may be applied with a calking gun or with a trowel. The sealant will cure to a tack-free condition in about 28 hours at 25° C, and will reach full cure in 72 hours at 25° C or in 48 hours at 50° C.

Properties of Cured Solid Sealant

The fully cured sealant, prepared and applied as described above is expected to have a peel strength of 4 lb/in. minimum at room temperature and 1.5 lb/in. minimum at -196° C (determined by the method of ASTM-D-1876). The sealant on an aluminum substrate was not visibly damaged by 5 cycles of immersion in liquid nitrogen and warming to room temperature.

Discussion

Both the foamed and the solid elastomeric sealants described above were judged, on the basis of the above evaluations, to be satisfactory for service at temperatures as low as -196°C and possibly satisfactory for service at even lower temperatures. The peel strengths cited above are conservative minimums; many of the laboratory-prepared samples had much higher peel strengths than those given above.

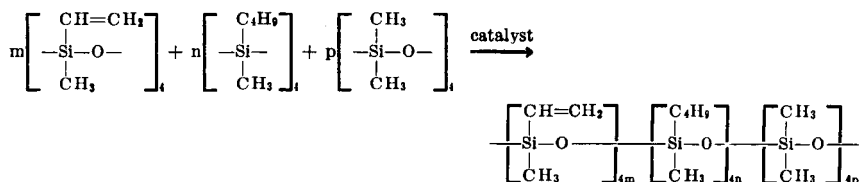
SYNTHESIS OF NEW POLYMERS FOR SEALANTS

As mentioned earlier, one of the objectives of the research program conducted by Hughes Aircraft Co. for Marshall Space Flight Center under Contract NAS 8-2428 was to develop new polymers that would be useful in sealant compositions for service at cryogenic temperatures. Since the portion of this program concerned with the evaluation of commercially available polymers had shown that the silicones and the polyurethanes were the most suitable of the many types of polymers investigated, efforts toward the synthesis of new polymers were concentrated on these two types. On the basis of a review of the literature and the investigation of commercial polymers, the investigators at Hughes concluded that a polymer should have a very low glass-transition temperature to possess the flexibility and toughness essential to good sealant performance at low temperatures. Preferably, the glass-transition temperature should be below the temperature of use of the sealant. It was also concluded that the polymer should be amorphous at the temperature of use, that there should be great mobility of segments of the polymer chains, and that there should be only a few cross-links in the polymer after curing. Because regularity in the molecular structure of a polymer favors crystallinity, it was concluded that irregularity in polymer structure was desirable. The silicones appeared to be a particularly interesting class of polymers for study because these polymers have inherently low glass-transition temperatures (refs. 49 and 50), and it appeared feasible to prepare silicone polymers having a high degree of structural irregularity which was expected to provide the desired low glass-transition temperature and low crystallinity. Hence, most of the experimental polymers prepared in the program were silicones.

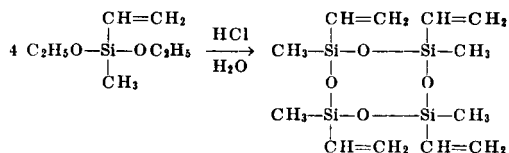
Silicone polymers were prepared with a wide variety of substituent groups on the silicon atoms. The polymers with methyl, ethyl, butyl, vinyl, and phenyl groups in various proportions were prepared and evaluated. The most satisfactory experimental polymer developed in this program and the only one that was evaluated extensively was a poly(methylbutylvinyl siloxane) cured with an alkoxysilane with dibutyltin dilaurate as catalyst.

Siloxane Polymers

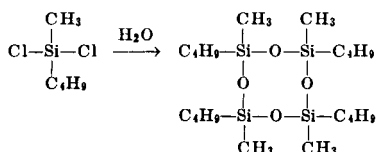
The general procedure used for preparing experimental silicone polymers was to mix cyclic-substituted siloxanes in the presence of a catalyst that caused the rings to open and the reaction to take place to form linear molecules. The polymerization reaction for the preparation of a poly(methylbutylvinyl siloxane) is represented by the following formula where m , n , and p are the molar proportions of each of the cyclic monomers:



The monomers were prepared by conventional methods. 2,4,6,8-Tetravinyl-2,4,6,8-tetramethylcyclotetrasiloxane was prepared, for example, by hydrolysis of vinylmethyldiethoxysilane.



In a similar manner, the butylmethyl cyclosiloxane was prepared by hydrolysis of a dichloride.

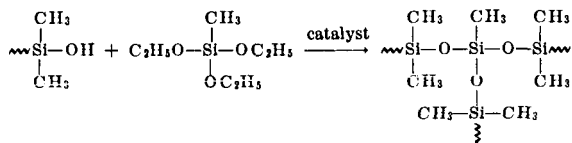


These hydrolysis reactions do not result in cyclic tetramers alone. Some cyclic trisiloxanes, cyclic pentasiloxanes, and even some cyclic hexasiloxanes are formed. No attempt was made to isolate the cyclic tetrasiloxanes from the mixtures since all of the cyclic siloxanes react similarly under polymerization conditions.

The preferred catalyst selected from among the several investigated was tetra-*n*-butylphosphonium hydroxide. When the cyclic siloxanes were heated for several hours at 120° C in the presence of this catalyst, the rings opened and the monomers combined to form linear polymers. When the temperature of the resulting polymers was raised to 200° C

for about 2 hours, the catalyst decomposed into neutral compounds (tributylphosphine oxide and butane), and the polymers were then stable.

The preferred method for curing these polymers was to combine them with a trifunctional alkoxy-siloxane, such as methyltriethoxy-siloxane, with dibutyltin dilaurate as a catalyst. This curing reaction occurs by ester interchange and may be represented as follows:



The curing of these silicone polymers with peroxide was studied in detail and was found to be unsatisfactory because the peroxide curing was inhibited by oxygen. To obtain curing with peroxides, it was necessary to exclude air from the polymer and catalyst mixture.

The techniques of monomer preparation and polymer synthesis developed in the research program carried out by Hughes Aircraft Co. made possible the preparation of a variety of silicone polymers for evaluation of flexibility at the temperature of liquid nitrogen and for adhesion to aluminum.

Of these polymers, a poly(methylbutylvinyl siloxane) was selected as the best for meeting the objectives of the program. The proportions of the various substituent groups on the silicon atoms (expressed as mole percent) were: methyl, 94.9 percent; butyl, 3.3 percent; and vinyl, 1.8 percent.

In a typical preparation of this polymer, 8.79 g of 2,4,6,8-tetra-vinyl-2,4,6,8-tetramethylcyclotetrasiloxane, 22.03 g of 2,4,6,8-tetrabutyl-2,4,6,8-tetramethylcyclotetrasiloxane, and 188.6 g of octamethylcyclotetrasiloxane were mixed and heated to 120° C in a nitrogen atmosphere. About 25 drops of catalyst solution were added, and the mixture was held at 120° C for several hours. The catalyst was a solution of tetrabutylphosphonium hydroxide (approximately 5 g in 10 ml). After polymerization had reached the desired stage as judged by the viscosity of the polymer, the temperature was raised to 200° C for 2 hours to decompose the catalyst. The polymer should be cured at room temperature by adding 4 parts of methyltriethoxysiloxane and 1 part of dibutyltin dilaurate to 100 parts of polymer.

Siloxanes as Curing Agents for Polyurethane

The investigators at Hughes Aircraft Company made some preliminary studies of the use of glycols containing siloxy groups as

curing agents for Adiprene L100. The combination of the polyurethane with a glycol having siloxy groups in its chain offered opportunities for producing a polymer with unusually good low-temperature properties because the bonds in the glycol units would be flexible and the substituents on the silicon atoms would inhibit crystallization. These preliminary experiments demonstrated that Adiprene L100 could be cured with 1,3-bis-(hydroxymethyl)tetramethyldisiloxane, and that the resulting polymer was a tough elastomeric material. The reaction between the siloxane and the Adiprene was extremely slow, and it was necessary to heat the material together for 3 days at 100° C to obtain the elastomeric polymer. These preliminary experiments demonstrated that the anticipated reaction occurred, but much additional work needs to be done before any conclusions can be drawn regarding the feasibility of making urethane polymers containing siloxane linkages. This is an area of research that deserves more attention.

Elastomeric Gaskets

NASA has conducted extensive studies of seals. Two programs of considerable interest to those working in the field of gaskets and other types of seal materials and equipment were carried out under Contract NAS 7-102.

Two important bibliographies (refs. 32 and 33) on static and dynamic seals and on gaskets were prepared by the Advanced Technology Laboratories of General Electric under this contract. These are important contributions, since there were no good bibliographies on the subject. The bibliography on the open literature (ref. 32) is particularly important, since it provides a thorough coverage of the English-language literature on dynamic and static seals published prior to mid-1962. The 1482 abstracts appearing in this report resulted from the review of 23 information-abstracting and publication-indexing services. All of the abstracting sources were searched back to their beginning. The abstracts appearing in this report are well written and informative. A very useful index to these abstracts is included in the report and it is a simple matter to locate abstracts of interest. The other bibliography (ref. 33) contains 682 abstracts, which are reproductions of those originally published. This bibliography is of less general interest than the one covering the open literature.

As a part of the same program, the Advanced Technology Laboratories of General Electric Co. also conducted a basic study of dynamic and static seals (refs. 34, 35, and 36). Much of this study was devoted to a theoretical appraisal of sealing methods and equipment, and the major emphasis was applied to dynamic seals. The discussion of static seals and gasket materials contains nothing new, but the report is an excellent sourcebook of information on the design of static seals and the selection of gasketing materials for various types of service.

The research work carried out by NASA and described in available reports has been concentrated on the development of gasket materials for use in contact with LOX (LOX-compatible gaskets). The gasket materials that are available or that can be developed readily with existing technology have probably been adequate for most of NASA's

needs, when used in closures of suitable design (refs. 37 and 38). However, no elastomeric gasket material that would perform satisfactorily when in contact with liquid oxygen was available, and research by NASA was required to develop a suitable material.

LOX-COMPATIBLE GASKETS

The requirements for an elastomeric gasket material that will function satisfactorily in LOX are formidable. Some of the problems are typical of those encountered in developing gaskets for use at cryogenic temperatures in any environment, and in addition the gasket material must be inert to LOX. This latter requirement practically limits the choice of polymeric materials to fluorocarbon polymers. All organic polymeric materials now available become harder and less resilient as the temperature is lowered, and their rates of contraction with decreasing temperature are greater than those of the metallic materials with which gaskets are most commonly used. Fluorocarbon polymers present some special problems because all of those presently known creep (deform) excessively under load, even at the temperature of LOX (ref. 36).

Because of an acute need for improved gaskets for LOX supply lines, NASA instituted a research program at Narmco Research and Development under Contract NAS 8-5053 with the objective of developing an improved material for such service. At the time this program began, a widely used gasket material for use with LOX in the NASA program was an asbestos-filled styrene-butadiene rubber (SBR) compound saturated with a liquid fluorocarbon. Although the SBR became hard and brittle at cryogenic temperatures, it would, if sufficiently compressed at normal temperatures before exposure to low temperature, generally provide a reasonably leak-free seal, and the liquid fluorocarbon protected the SBR from LOX.

After surveying the existing technology, the Narmco investigators concluded that the only potentially useful polymers for their purpose were fluorocarbon polymers and selected tetrafluoroethylene (TFE) and fluorinated ethylenepropylene (FEP) polymers for extended study. It was known that gaskets made of unmodified polymers of these types were not very satisfactory at cryogenic temperatures because of excessive creep and, also, that the incorporation of powdered fillers or short filaments in these polymers would not result in sufficient reduction of creep (ref. 39). However, gaskets made from these polymers and combined with woven glass fabric for reinforcement offered promise (ref. 37).

The research effort in this program was concentrated on development of a suitable laminate of glass fabric and fluorocarbon polymer (ref. 40). The laminates developed as the optimum products were

judged to have good prospects for being satisfactory for cryogenic applications, and they were, in some respects, novel structures. The technique developed for producing these laminates was to make a sandwich-like structure by applying the polymer to both sides of the glass fabric without allowing it to penetrate the fabric or to encase the glass filaments. With this technique, the mechanical compressibility of the glass fabric was largely retained, and, since the resilience of the glass fabric was not substantially affected by temperature, this structure provided definite advantages in the performance of gaskets at low temperatures.

Two types of gasket structures were developed to see whether the mechanical compressibility of glass fabric could be used to improve the low-temperature performance of gaskets.

To make one type of structure, alternate layers of glass fabric and sheets of tetrafluoroethylene polymer were laid together with the fabrics arranged so that the yarns of the fabric in each layer were at an angle to those in the nearest layers. This arrangement was found to be superior to that with the yarns of successive fabric layers parallel. The laminates were formed in a hydraulic press with platens heated to 425° C. The laminating pressure was 500 psi and pressing time at 425° C was 30 min. The laminates were cooled under pressure to 205° C and then removed from the press and quenched in water. Quenching was desirable because it minimized the crystallinity in the tetrafluoroethylene polymer, with consequent improved flex life (ref. 41). Since the glass fibers in these laminates were not completely surrounded by the polymer, the edges of sections cut from the laminate were not sealed and liquid could soak into the gasket material. To prevent this, gaskets cut from the laminates were either encapsulated in fluorinated ethylene-propylene polymer, or the cut surfaces were coated with this polymer.

The second type of gasket structure developed in the Narmco program was a modification of that described above. In this type, multiple layers of glass fabric were encapsulated in polymer film.

The encapsulated, or envelope, gasket was prepared by cutting several pieces of glass fabric in the shape and size desired for the gasket, placing one sheet of Teflon FEP under the pieces of fabric and another sheet on top of them, and sealing the Teflon film around the fabric by heating in a press. In this design, there was no plastic between the layers of fabric, and the mechanical properties of the multiple plies of fabric provided the back stress required to maintain a tight seal.

An evaluation technique used for preliminary screening of gasket materials in the work done for NASA under Contract NAS 8-5053 is of sufficient general interest to warrant description here. Gaskets

were compressed under a load of 3000 psi in a conventional test machine. The deflection of the gasket was measured and load vs. deflection data were recorded. The loading and unloading cycles were repeated several times and a record of the load vs deflection was made during each cycle. In most of the work reported these measurements were made at a temperature of -196°C . The areas under load-deflection curves were calculated and taken as measures of the energy absorbed by the gasket material when compressed. It was assumed that the materials showing the highest energy-absorption values and minimum fall-off in energy absorption with cycling were the best candidate materials. Figure 6 shows the energy-absorption data for three gasket materials as a function of the number of compression cycles. The materials evaluated were a good-quality glass-reinforced laminate, a glass-reinforced laminate of unacceptable

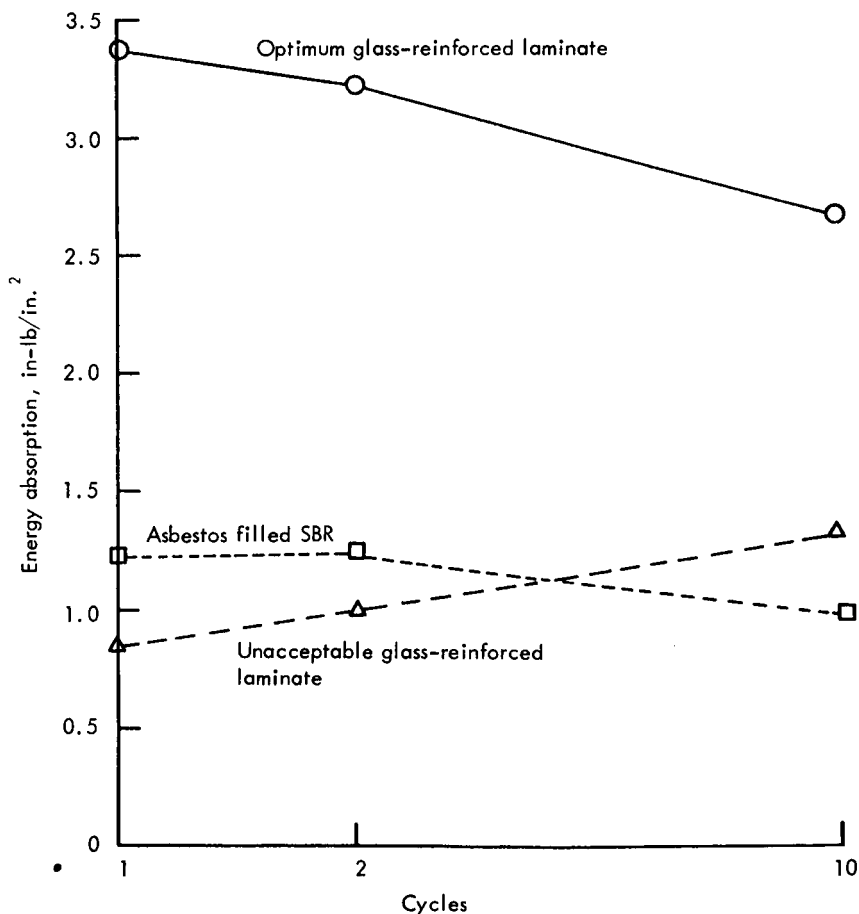


FIGURE 6.—Energy absorption of gaskets.

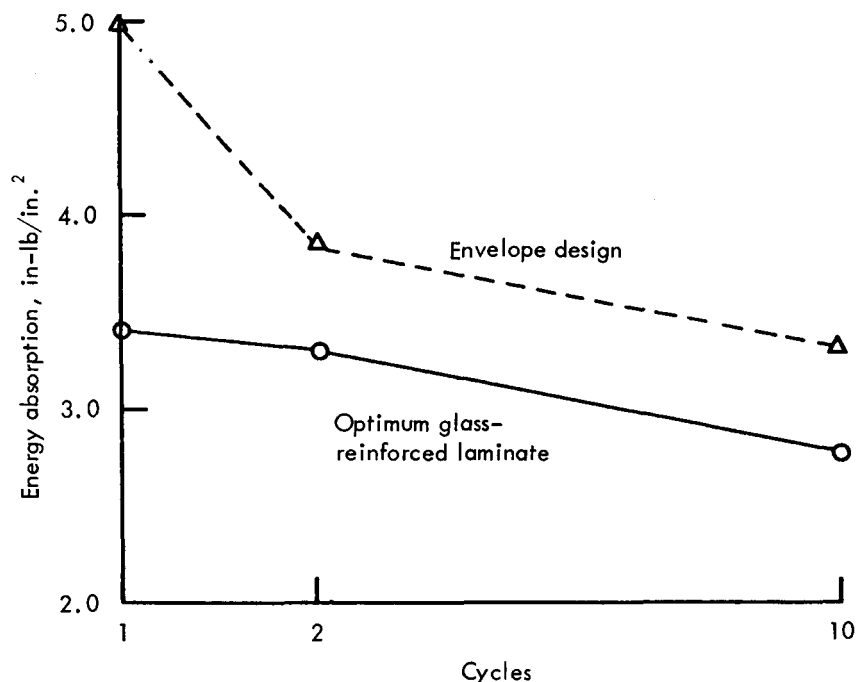


FIGURE 7.—Energy absorption of gaskets.

quality, and a gasket made of styrene-butadiene rubber reinforced with asbestos fiber and saturated with a liquid fluoroethylene polymer. This last gasket material was commonly used for LOX-compatible service prior to the development of better materials.

A comparison of the energy-absorption values for the laminated gasket material and the encapsulated glass fabric materials described above is shown in figure 7. The encapsulated glass-fabric material was slightly superior to the laminated product in energy-absorption characteristics. However, it should be recognized that the laminated gasket material had much better strength characteristics and would be preferred for most uses.

RESEARCH ON NEW POLYMERS

Fluorocarbon Polymers

NASA has sponsored a program of basic research on polymers with the objective of developing new types of elastomers that are serviceable in contact with LOX. This research program, carried out under Contract NAS 8-5352 by Peninsular Chemresearch, Inc., has been concerned with the synthesis of new types of fluorinated polymers. The latest report at the time of this survey indicated that

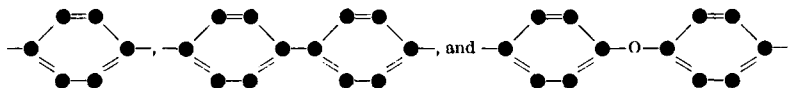
some new polymers had been prepared in small quantities (a few grams) (refs. 42 and 43). The properties of these polymers were not reported, and, consequently, no appraisal of their potential utility can be made. However, the results of this program are expected to be a definite contribution to polymer technology.

Several new monomers were prepared in this program (ref. 43); three of special interest were: $\text{CF}_3\text{OCH}=\text{CF}_2$, $\text{CF}_3\text{OCF}=\text{CHF}$, and $(\text{CF}_3\text{O})_2\text{C}=\text{CF}_2$. Polymers were prepared from each of these monomers by copolymerization with vinylidene fluoride, $\text{CF}_2=\text{CH}_2$, and, in some instances, with vinyl fluoride, $\text{CFH}=\text{CH}_2$, and tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$. All polymerizations were initiated by small doses of gamma radiation.

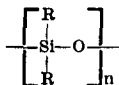
As indicated earlier, the polymers had not been prepared in sufficient quantity to permit evaluation of their properties. But it is significant that procedures for producing these new polymers have been developed, and it is anticipated that further work with them will result in the development of useful new products.

Silicon-Containing Polymers

During the past few years, many new types of silicon-containing polymers have been developed. Some of these are elastomeric materials that may ultimately prove useful in gasket materials for high-temperature service. NASA has made notable contributions to the development of these polymers. Silicon-containing polymers incorporating thermally stable organic groups, such as

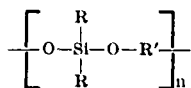


in the polymer backbone, have received particular attention. Such polymers differ distinctly from the well-known silicone polymers that have the general formula

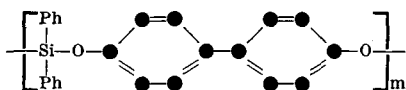


and have only silicon and oxygen atoms in the backbone of the polymer.

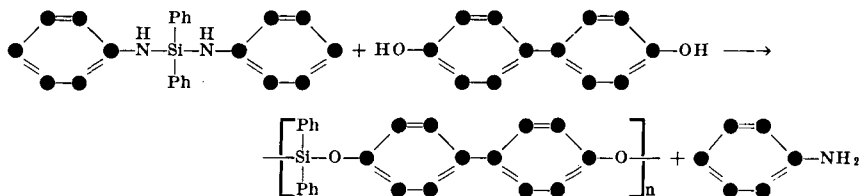
Curry and Byrd, at Marshall Space Flight Center, prepared high molecular-weight polymers of the general type



by the reaction of silyldiamines and various organic diols (ref. 44). The most desirable of the various polymers prepared by these investigators was poly(4,4'-bisoxybiphenylene diphenylsilane)



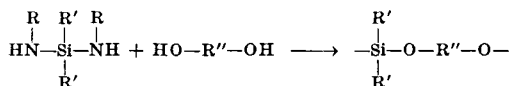
which was synthesized by the melt polymerization of bis(anilino)-diphenylsilane and *p,p'*-diphenol.



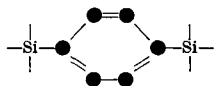
This polymer and similar polymers prepared by Curry and Byrd were tough and fairly flexible materials, but they were not elastomeric. The poly (4,4'-bisoxydiphenylene) diphenylsilane described above was thermally stable for short periods at 600° C and for long periods at 400° C.

Many aspects of the chemistry of polymer formation from silicon-nitrogen compounds have been explored in the research at Southern Research Inst. under Contract NAS 8-1510. Some of the experimental polymers that were produced were elastomeric and they retained a good degree of elasticity after exposure to temperatures as high as 400° C.

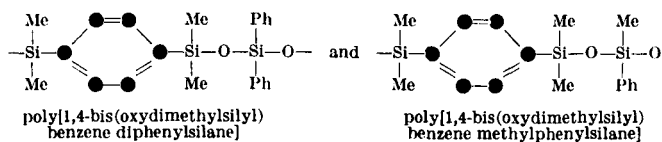
Some of the most interesting of the elastomeric polymers produced at Southern Research Inst. were made by variants of the diol-diaminosilane reaction used by Curry and Byrd. For example,



permits incorporating into the polymer backbone the silphenylene group



This group was introduced by the use of either 1,4-bis(dimethylhydroxysilyl)benzene or 1,4-bis(methylaminodimethylsilyl)benzene as the monomer in the above reaction. The toughest and most thermally stable of the various polymers that were made were:



The structures of some of these polymers and the reactions used to prepare them are shown in figure 8 (ref. 45).

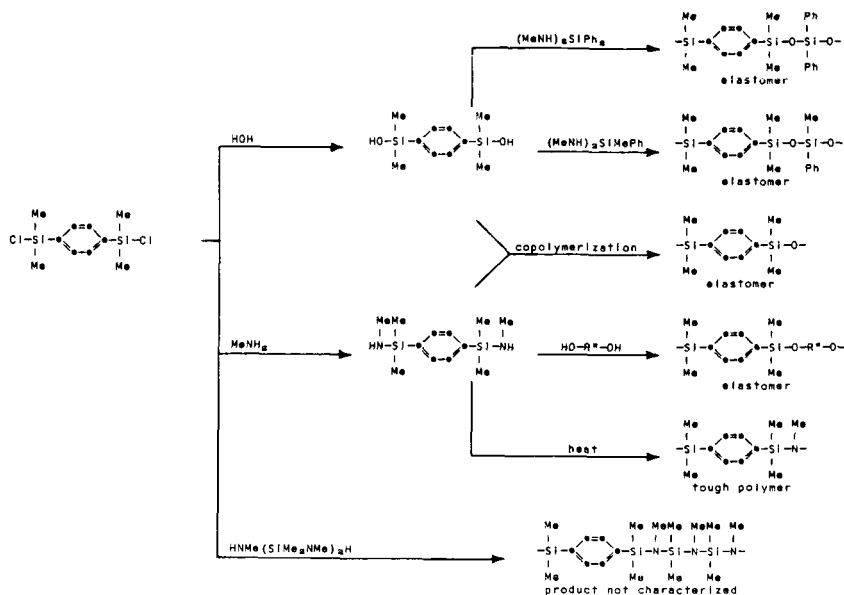


FIGURE 8.—Routes to silphenylene polymers.

The prospects are good that the programs on silicon-nitrogen chemistry being carried out by NASA and others will ultimately result in the development of improved elastomeric polymers that will be useful in gaskets for high-temperature service.

NEW TECHNIQUES AND FACILITIES

Miniature Stress Transducer

In order to measure internal stresses in materials, the Jet Propulsion Laboratory has made use of a miniature stress transducer with directional capability (ref. 46), and this device should be extremely useful in studying stress in gaskets. These transducers are only 0.1 inch in length and 0.05 inch in diameter, and this small size should make it possible to install them in gaskets and study the stresses that gaskets undergo while in actual service. Initial stress and stress decay in the

gaskets could be monitored to provide extremely useful information regarding changes in the characteristics of the gaskets during service. Normally the stress-decay properties of gasket materials are measured in the laboratory under simulated service conditions, and frequently the data obtained do not accurately reflect performance in service.

The usefulness of these small transducers in studying gaskets has not been demonstrated, but they appear to be capable of providing much more accurate information on gasket performance than is possible by the techniques now in use.

Gasket Testing Facility

The Marshall Space Flight Center has instituted a study of performance during aging of a variety of rubber and plastic gasket materials installed in simulated flight hardware (ref. 47). As this program is still in progress, it is premature to report any results. The program is certain to provide much useful data on the performances of a variety of materials. Although no results can be reported, mention is made of this program to alert interested parties to be on the lookout for the results.

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Unclassified NASA and NASA-sponsored publications may be consulted at these Federal regional technical report centers: University of California, Berkeley; University of Colorado Libraries, Boulder; Library of Congress; Georgia Institute of Technology, Atlanta; The John Crerar Library, Chicago; MIT, Cambridge, Mass.; Linda Hall Library, Kansas City, Mo.; Columbia University, New York, N.Y.; Carnegie Library of Pittsburgh; Southern Methodist University, Dallas; and the University of Washington Library, Seattle.

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